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ATMOSPHERIC REACTION STUDIES IN THE LOS ANGELES BASIN

PHASE II

DATA ANALYSIS AND METHODS IMPROVEMENT

COORDINATING RESEARCH COUNCIL, INC.

(APRAC Project No. CAPA-7-68)

NATIONAL AIR POLLUTION CONTROL ADMINISTRATION

(NAPCA Contract No. CPA 22-69-19)

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A comprehensive survey of the atmosphere of the Los Angeles Basin was conducted during the period August 22 to November 14, 1968. A large number of contaminants were determined continuously and periodically, and readings of pertinent meteorological factors were made at two ground level sites and in an aircraft at several altitudes above the ground sites. Mobile trailer-type laboratories were used in this study. The trailers contain instrumentation for continuous monitoring of a number of contaminants, photochemical products and meteorological parameters.

The pollutants measured included carbon monoxide, oxidant, ozone, nitric oxide, nitrogen dioxide, total hydrocarbons, individual C_1 to C_{10} hydrocarbons, peroxyacetyl nitrate, formaldehyde, acrolein and total aliphatic aldehydes. The meteorological elements monitored included temperature, relative humidity, wind speed and direction, and ultraviolet radiation intensity. The most significant advance was the chromatographic determination of more than 100 individual hydrocarbons.

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Atmospheric Reaction Studies in the Los Angeles Basin

Phase II

Data Analysis and Methods Improvement

for

Coordinating Research Council, Inc.

and

National Air Pollution Control Administration

(Contract No. CPA 22-69-19)

by

SCOTT RESEARCH LABORATORIES, INC.
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SUMMARY

The aerometric data collected by Scott in the Los Angeles Basin during the Fall of 1968 was analyzed to study the relationships among the chemical and meteorological parameters measured. Emphasis was placed on defining the formation rates of the products of atmospheric chemical and and photochemical reactions, especially nitrogen dioxide and ozone. The data analysis was also performed to aid in the design of the 1969 field program.

The study was concentrated on the empirical relationships which connect the outputs of the atmospheric system, i.e. the photochemical products, to the inputs represented by pollutant emissions and ultraviolet radiation. This approach offered the possibility of greatly facilitating the derivation of relationships which could be used to evaluate the effects of controlling the system inputs.

The concentrations of many contaminants followed similar diurnal patterns. Good correlation was found among carbon monoxide, acetylene and total C_5 to C_{10} hydrocarbons. A close relationship was also found among methane, ethane and propane, but these hydrocarbons did not correlate well with total C_5 to C_{10} hydrocarbons. Different primary sources were indicated.

The concentrations of gasoline range olefins found in the atmosphere before photochemical reactions started were only half of those expected based on analyses of gasolines in use during the period.

The ratio of carbon monoxide to nitrogen oxides was subject to wide variation from day to day. However, the hourly averages for the entire period showed little change with time of day. The average carbon monoxide to nitrogen oxides ratio was 30 which was the same as reported for exhaust from

The oxidant appeared to increase at a faster rate during transport than when the air mass remained in the Huntington Park area.

The airborne measurements revealed much information about the three-dimensional aspects of the Los Angeles Basin. The vertical profiles showed that the base of the temperature inversion was at an approximate altitude of 700 feet above sea level during the morning. The fresh inputs to the atmosphere were confined below this level. Oxidant was higher within the inversion than below it during the early morning despite the lower concentrations of reactants present. As a typical day progressed, oxidant increased rapidly in the air below the inversion. The inversion base began to rise and the sea breeze started. The smog front was visible from aloft as it moved toward the El Monte site. By mid-afternoon the inversion either broke up completely or rose to an altitude above 1500 feet. The composition of pollutants in the atmosphere was then quite uniform between ground level and 1500 to 2500 feet above sea level.

The work dealing with improvement of methods applicable to atmospheric analysis concentrated on techniques for atmospheric nitrogen compounds, hydrocarbons, nitrogen oxides and oxidants. Among the achievements of this effort were automation of the electron capture chromatograph used for peroxyacetyl nitrate and development of an improved technique and calibration standard for use with it. The C_1 to C_{10} hydrocarbon analysis was also improved by revising the chromatograph flow system, developing a purifier for the carrier gas and identifying additional chromatographic peaks. The stability of hydrocarbons and nitrogen oxides in Tedlar bags was found to be satisfactory for use in airborne work. Other instrumentation for chemical and meteorological parameters was checked out, revised or repaired where necessary and made operational for the start of the 1969 field survey.

1. INTRODUCTION

This final report describes the work performed on Phase II of APRAC Project CAPA-7-68, "Atmospheric Reaction Studies in the Los Angeles Basin" (Contract No. CPA-22-69-19). Phase II consisted of two major activities: analysis of the aerometric data collected by Scott during the fall of 1968 and development of improved methods of chemical analysis applicable to the 1969 field survey and other future aerometric studies.

The purpose of the data analysis was to study the relationships among the chemical and meteorological parameters measured in the 1968 field survey of the Los Angeles Basin[1,2] in order to define the formation rates of various photochemical products, especially nitrogen dioxide, oxidant and ozone in terms of these parameters. Additional relationships were studied to shed light on emissions sources, reaction times and the overall behavior of the atmospheric system. The data analysis was also conducted to aid in the design of the 1969 field program by providing a firmer basis for evaluating the most important factors to be measured, the critical periods during which measurements should be made and the location of sampling points.

The methods development was undertaken to improve analytical techniques which did not produce satisfactory results in the 1968 field survey or devise alternate methods, to expand other procedures to make them capable of providing additional useful data, and to validate the performance of the instrumentation and procedures employed in the field work. Emphasis was placed on analysis of nitrogen compounds and individual C_1 to C_{10} hydrocarbons. Most of the work was performed in Scott's Plumsteadville laboratory using the same instrumentation and equipment that had been located in the

Scott mobile laboratory used to obtain data at the El Monte site in the 1968 Los Angeles Basin survey.

2. ANALYSIS OF DATA FROM 1968 LOS ANGELES BASIN SURVEY

2.1 GENERAL APPROACH TO THE ATMOSPHERIC SYSTEM

The study described in this report was limited to an empirical analysis of aerometric data collected by Scott in the 1968 survey of the Los Angeles Basin. Since nearly all of the 1968 data were collected at two fixed sites, the analysis was limited to the sub-systems representing the atmosphere in the immediate vicinity of the sampling points rather than to the entire Los Angeles Basin atmosphere. The relationship between the sub-systems at the two sites was also investigated. While no attempt was made to model the Basin atmospheric system, a generalized concept of the atmospheric system was desirable as an aid in searching for relationships among the variables measured.

There are three distinct aspects which must be considered in defining the changes in composition and concentration which take place in an atmospheric system, namely input of pollutants into the system, chemical reactions and physical processes within the system, and transport of reactants and products out of the system. All variations in atmospheric concentrations of the pollutants measured in the field survey were combined effects of these three aspects, so that while the data analysis deals essentially with atmospheric chemical reactions, the true rate of each reaction cannot be determined without a knowledge of pollutant inputs and transport characteristics.

The concentration of each of the literally hundreds of individual pollutants present in the atmosphere is constantly changing. Fresh material is continually being added to the atmosphere but its composition and rate

of addition are subject to variation as the relative strength of each pollutant source follows its diurnal pattern. The rate of transport out of the system is likewise changing as wind speed, inversion height and other meteorological factors vary. Finally, the rate of each of the hundreds of separate chemical reactions changes as concentrations, radiation intensity and temperature change. When the additional complexities of vertical and horizontal non-homogeneity are considered, the system becomes too chaotic to be treated in its entirety. Therefore, the system must be segmented and simplified.

Study was concentrated on the empirical relationships which connect the outputs of the system, i.e. the photochemical products, to the inputs represented by contaminant emissions and ultraviolet radiation. This approach made it possible to bypass the kinetics of individual reactions and disregard the involvement of such intermediates as zwitterions and free radicals. This approach offers the possibility of greatly facilitating the derivation of relationships which could be used to evaluate the effects of controlling the various system inputs.

It was decided that the data were best analyzed by following the short term changes in the atmosphere rather than daily or seasonal averages. The latter identify the meteorological conditions which favor heavy smog formation but tend to mask the effects of individual contaminants which are of greater interest because they can be potentially controlled. The half hourly averages presented in the data file were inadequate to define rates of reaction during periods of rapid change, and it was necessary to refer to the continuous strip charts to obtain the desired precision.

The overall strategy was thus to develop pertinent relationships

which defined the formation rate of each photochemical product and the extent to which it accumulated in the atmosphere. These individual relationships could then be tied together into sub-models and models in future work.

2.2 CONTAMINANT CONCENTRATIONS, DIURNAL PATTERNS AND INTERRELATIONSHIPS

The pollutants present in the Los Angeles Basin atmosphere can be divided into two categories, those emanating directly from emission sources and those formed through chemical reactions occurring in the atmosphere. This section considers those contaminants in the first category which were measured in the 1968 field survey. They include carbon monoxide, individual C_1 to C_{10} hydrocarbons, nitrogen oxides and aldehydes. The reaction products such as ozone, oxidants, and nitrogen dioxide and aldehydes produced by atmospheric reactions are discussed in subsequent sections.

The comprehensiveness of the aerometric data collected at the two ground sites permits a detailed look into contaminant concentrations, their day-to-day and within day variations, and their sources. While the data apply only to the site at which they were obtained, the relative remoteness of both sites from known high emissions sources makes it reasonable to assume that the atmosphere at each site was typical of that in a relatively wide area around the site.

The sources of contaminants present in the air during the early morning period are of considerable interest because it is these contaminants which are trapped by inversions and irradiated to produce the peak concentrations of ozone and other photochemical products noted in the afternoon. On the other hand, previous studies[3] have shown that afternoon emissions cause only a slight rise in contaminant concentrations and usually play a

minor role in photochemical processes.

CARBON MONOXIDE

Carbon monoxide does not participate in photochemical reactions. For this reason and because it has been estimated that as much as 95% of the carbon monoxide in the Los Angeles Basin atmosphere comes from automotive exhaust emissions, carbon monoxide appeared potentially valuable as an atmospheric tracer for auto exhaust.

In order to test the above assumption, the relationship between carbon monoxide and acetylene, a photochemically inert hydrocarbon also believed to be contributed almost exclusively by auto exhaust, was investigated using data from the Huntington Park site. Linear regression analysis of 97 simultaneous measurements of carbon monoxide and acetylene concentrations yielded the following relationship:

$$CO\ (ppm) = 113\ C_2H_2\ (ppm) - 0.06$$

Correlation Coefficient = 0.967

Standard Error of Estimate = 1.98 ppm

The carbon monoxide to acetylene ratio of 113 is close to the value of 120 generally accepted for exhaust from pre-1966 cars (based on 3% carbon monoxide and 250 ppm acetylene).

The high correlation between carbon monoxide and acetylene concentrations and the fact that they were present in essentially the same ratio as found in auto exhaust supports the assumption that exhaust is the major source of these contaminants. However, the quantities of carbon monoxide and acetylene emitted to the atmosphere from other combustion processes of fuels must be determined before the relative contributions of vehicular and

other sources can be firmly established.

In the correlation study of carbon monoxide and acetylene the correlation was not nearly so good when the carbon monoxide values were obtained by interpolating the half hour averages to the time that the acetylene sample was collected. The good correlation found above resulted from reading the carbon monoxide concentration from the strip chart records. Subsequent studies of other parameters confirmed that when one parameter was determined using an instantaneous sample, much better correlation was obtained when the second parameter was read simultaneously. This finding points out that values for continuously recorded parameters should be reported for intervals shorter than the thirty minutes used for the 1968 data.

The concentration of carbon monoxide at Huntington Park ranged from <1 to 37 ppm. The highest concentrations usually occurred between 0630 and 0730 PST although high overnight concentrations were frequently found in November.

The highest average concentration of carbon monoxide over one day was 12 ppm.

The averages for individual days of the week were:

Sunday	4.4	
Monday	3.3	
Tuesday	4.0	
Wednesday	5.2	
Thursday	4.7	
Friday	2.8	
Saturday	5.0	
Avg.	4.2	$\sigma = 0.79$

Previous monitoring programs had found that carbon moroxide was lower on Saturday and Sunday than on weekdays because of the lower traffic volume. The present data do not bear this out in that there is no significant difference in the averages for different days of the week. This means either that the week-end traffic volume in the Huntington Park area was not significantly lower than that on weekdays or that daily carbon monoxide concentrations were more a function of meteorological conditions than of traffic density.

The highest carbon monoxide concentration measured at El Monte was 14 ppm. This maximum was found within one-half hour of the period high of 37 ppm at Huntington Park. The carbon monoxide at El Monte was generally from one-third to one-half that at Huntington Park during the morning (0900 to 1100 PST). The El Monte concentration decreased steadily during this period and then showed a sharp upsurge when the sea breeze brought in the polluted air from the southwest. This second maximum, which usually occurred between 1200 to 1400 PST, seldom exceeded the early morning maximum for that day. There are insufficient data points for El Monte to develop additional averages or trends.

HYDROCARBONS

Hydrocarbons are major participants in the chemical reactions occurring in the Los Angeles Basin atmosphere. The availability of data for approximately 100 individual hydrocarbons covering the range from C_1 to C_{10}, nearly all of which are photochemically reactive to some degree, provided sufficient information for a study of sources and reaction rates. This section is limited to a study of composition and sources while the investigation of reaction rates is covered in a later section.

Two chromatographic columns were used for hydrocarbons, one for

C_1 to C_4 and the other for C_5 to C_{10}. The correlation between n-butane which was determined with the first column, and n-pentane, which was determined with the second column, was investigated to verify that the data from the two columns were compatible. The relationship found using 101 data points from Huntington Park was:

$$n\text{-}C_4H_{10}\ (ppb) = 2.18\ n\text{-}C_5H_{12}\ (ppb) + 10.9$$

Correlation Coefficient = 0.950

Standard Error of Estimate = 16.2 ppb

The data from the two columns are thus reasonably compatible. The concentrations of n-butane are comparable to those found in downtown Los Angeles in 1967[3] and the ratio of pentane to butane is in agreement with results reported by Stephens[4,5] for samples collected in the Los Angeles Basin and other sections of California. The intercept probably represents background butane emanating from a second source containing much less pentane than the primary source.

The data for total concentration of C_5 to C_{10} hydrocarbons are less accurate at low levels than at high levels because the peaks of some minor components were too small to be counted by the integrator and occasional spurious peaks were counted. It was hypothesized that the sum of a few hydrocarbons, normally present in high concentration and representative of the various carbon numbers and classes, would provide a better measure of the total C_5 to C_{10} hydrocarbons than would the sum of all the detected compounds. The six hydrocarbons selected were n-pentane, 2-methylpentane, 2-methylhexane, methylcyclohexane, toluene and m + p-xylene. The relationship obtained was:

Total HC (ppb) = 2.06 Σ 6HC (ppb) + 8.9

Correlation Coefficient = 0.993

Standard Error of Estimate = 37.2 ppb

A study of the outliers showed that all were the result of either spurious or uncounted peaks. This demonstrated that the sum of the six hydrocarbons was a slightly more reliable measure of total C_5 to C_{10} hydrocarbons than was the sum of all the compounds listed in the data printouts.

Individual correlation of acetylene and carbon monoxide with the total C_5 to C_{10} hydrocarbons and with the sum of the above six hydrocarbons gave the following relationships:

	Correlation Coefficient	Standard Error of Estimate
C_2H_2 (ppb) = 0.188 Total HC (ppb) + 2.81	0.936	23.2 ppb
C_2H_2 (ppb) = 0.581 Σ 6 HC (ppb) + 3.98	0.936	23.1 ppb
CO (ppm) = 22.0 Total HC (ppm) - 0.09	0.961	2.06 ppm
CO (ppm) = 68.0 Σ 6 HC (ppm) + 0.04	0.963	2.03 ppm

The high correlation between carbon monoxide and the total C_5 to C_{10} hydrocarbons does not necessarily prove that they have a common source, namely auto exhaust. First, the degree of correlation attributable to the atmospheric dispersion rate, which tends to cause all contaminants to increase and decrease at the same rate, must be factored out. Second, detailed data on exhaust composition must be studied to determine if the ratios of carbon monoxide to the various hydrocarbons with low photochemical reactivity are similar for exhaust and the atmosphere. Adequate data are not available so no conclusions

can be drawn. However, the day to day variations in atmospheric composition noted both with regard to hydrocarbon class and molecular weight range suggest more than one major source of C_5 to C_{10} hydrocarbons. If vehicular exhaust were the only major contributor, the hydrocarbon composition would not change with time except through photochemical reactions. This is true because the large number of vehicles contributing to each sample would be expected to normalize any variations due to vehicle or fuel differences.

The concentrations of methane, ethane and propane did not exhibit nearly as good correlation with the total C_5 to C_{10} hydrocarbons as was found for acetylene. In Figures 2-1 through 2-4, the data for these four hydrocarbons are plotted against the sum of the 6 hydrocarbons, which were found to represent the total C_5 to C_{10} hydrocarbons. The much larger scatter for methane, ethane and propane than for acetylene is quite evident. The linear relationship between methane and ethane and propane is illustrated in Figures 2-5 and 2-6. This suggests a common source for these three contaminants. The methane concentration of approximately 1.4 ppm known to be present in the natural atmospheric background is evident from the intercepts of the methane plots.

These findings are in line with those from previous studies[3,4]. It has been proposed by Stephens[4] that these light paraffins result primarily from natural gas leaks and from evaporative processes. Still, the concentrations of propane were higher than he could readily explain because the atmospheric propane concentration was approximately half the ethane while in natural gas it is only one-fifth the ethane. It is apparent that additional source data are needed to clear up the mystery of the excess propane. However, the relatively low reactivity of propane minimizes the importance of solving

Figure 2-1
Sum of 6 Representative C_8 - C_{10} Hydrocarbons
vs
Acetylene
Huntington Park

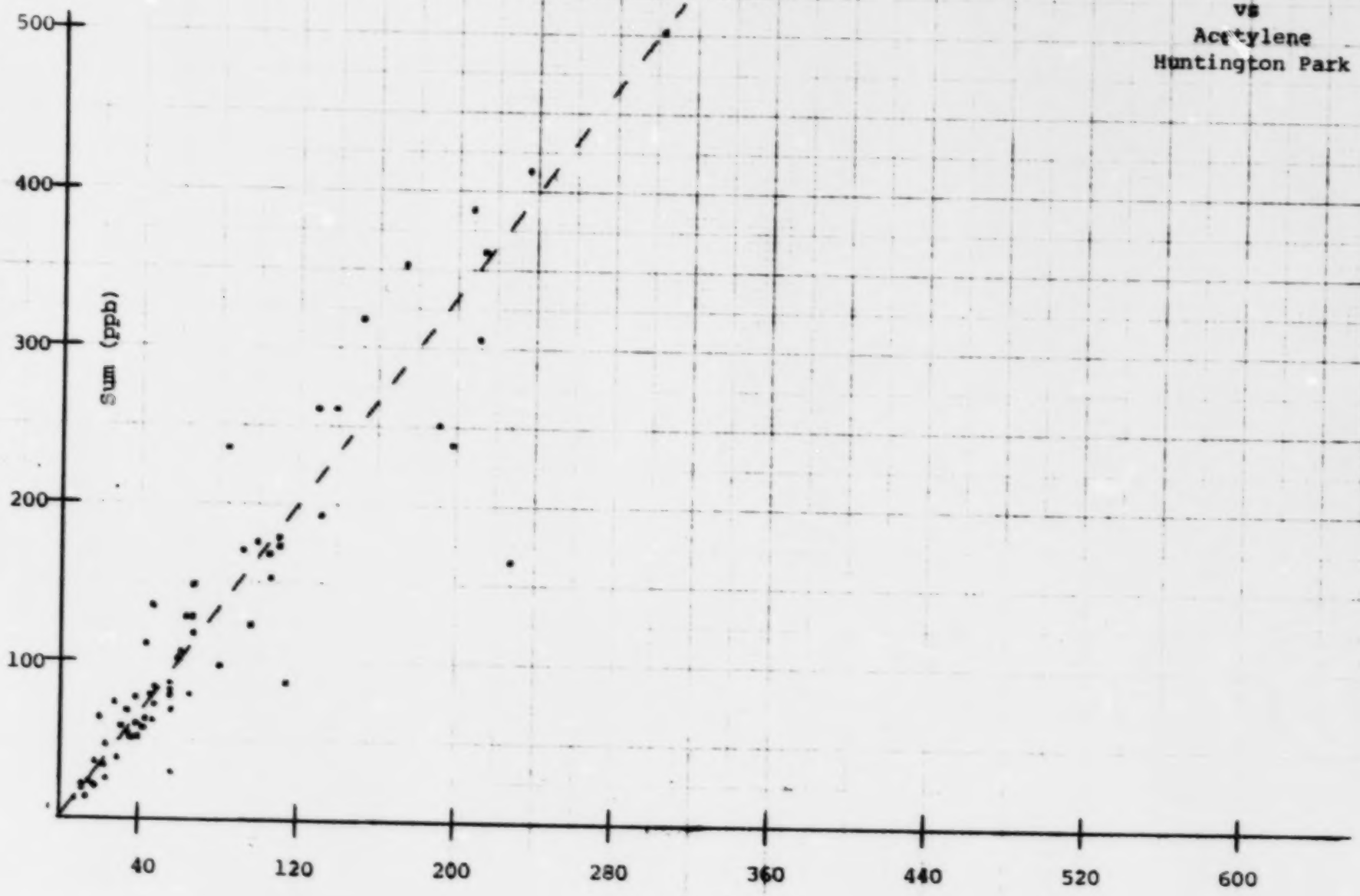


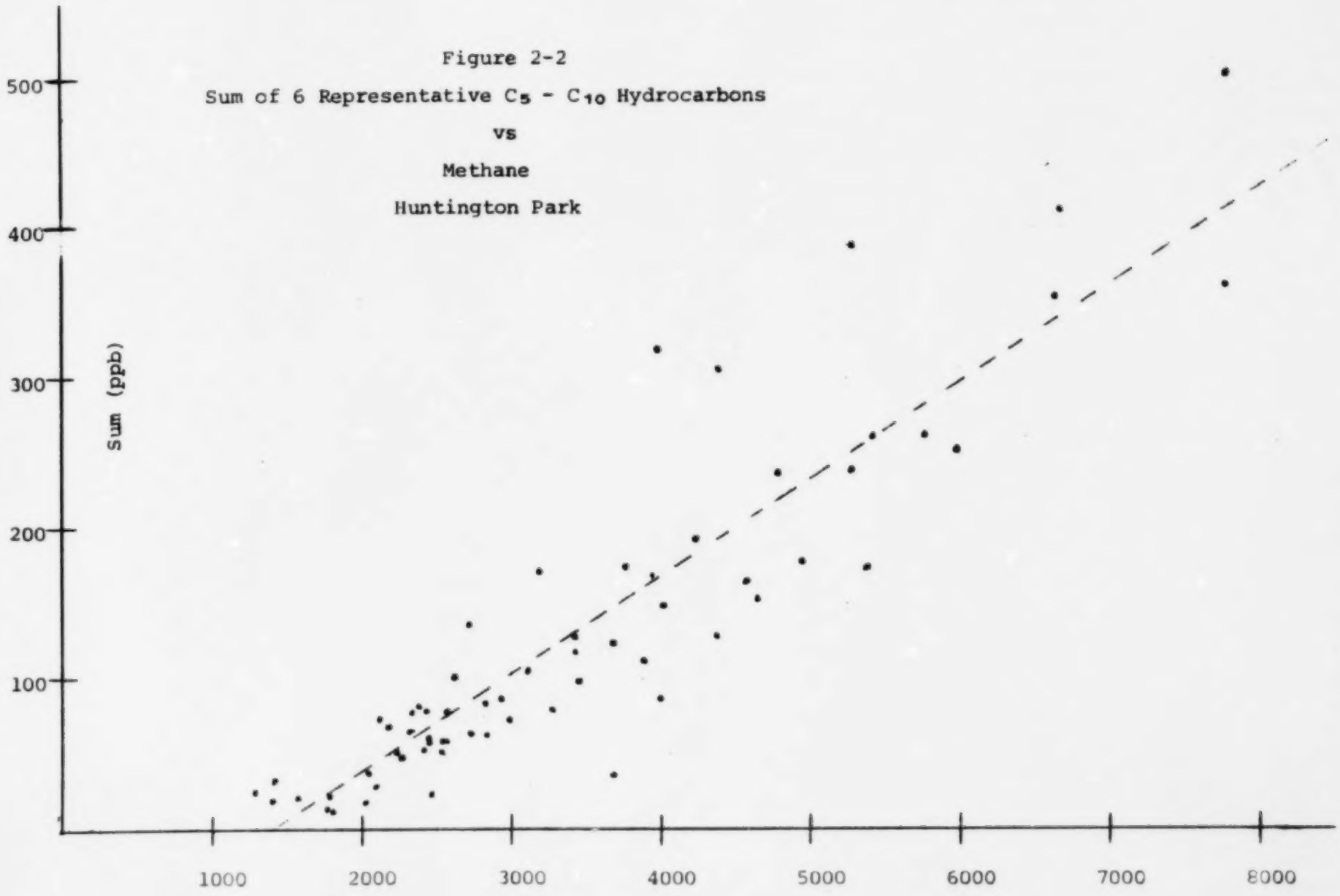
Figure 2-2

Sum of 6 Representative C_5 - C_{10} Hydrocarbons

vs

Methane

Huntington Park



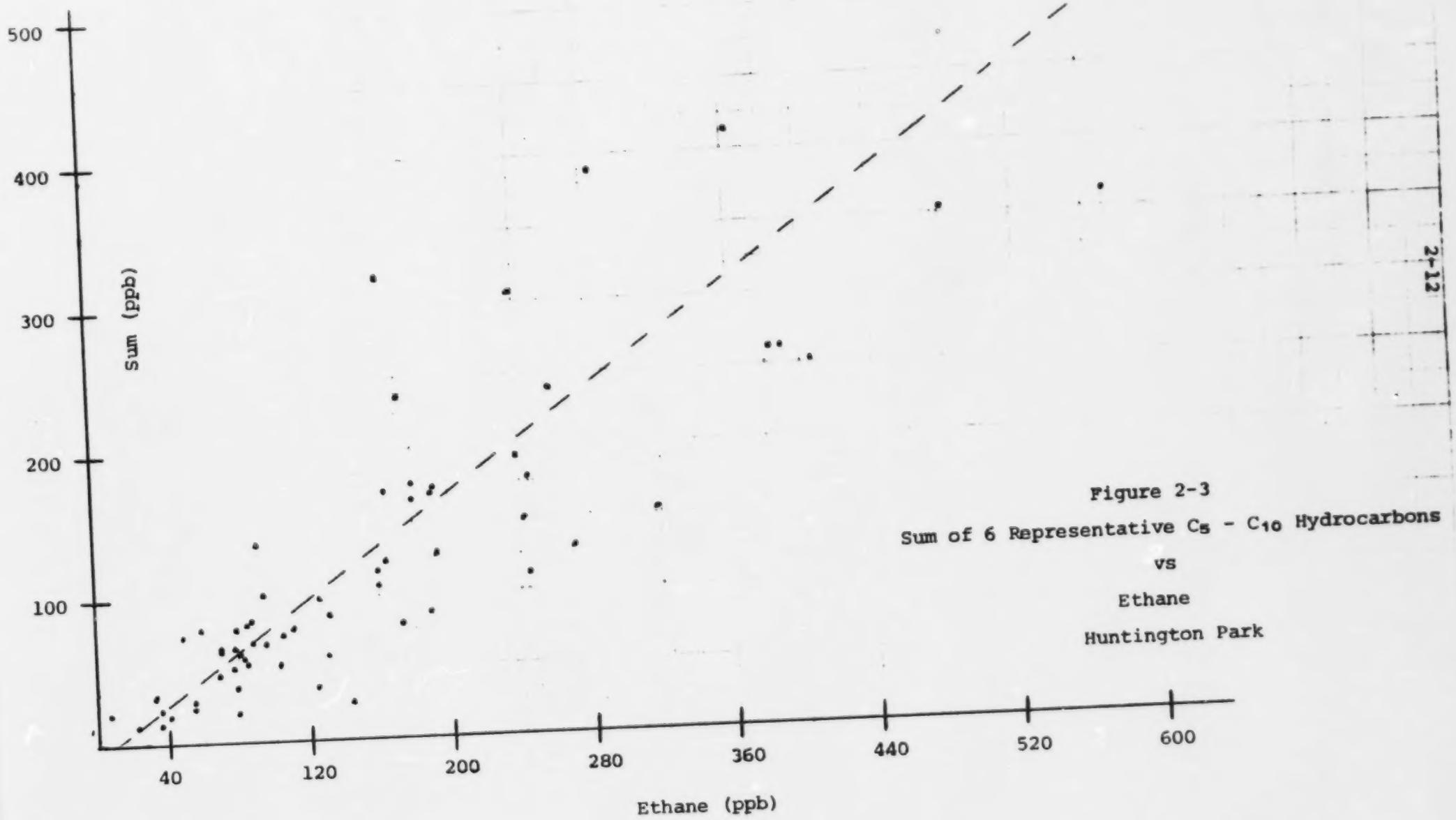


Figure 2-3

Sum of 6 Representative C_5 - C_{10} Hydrocarbons

vs

Ethane

Huntington Park

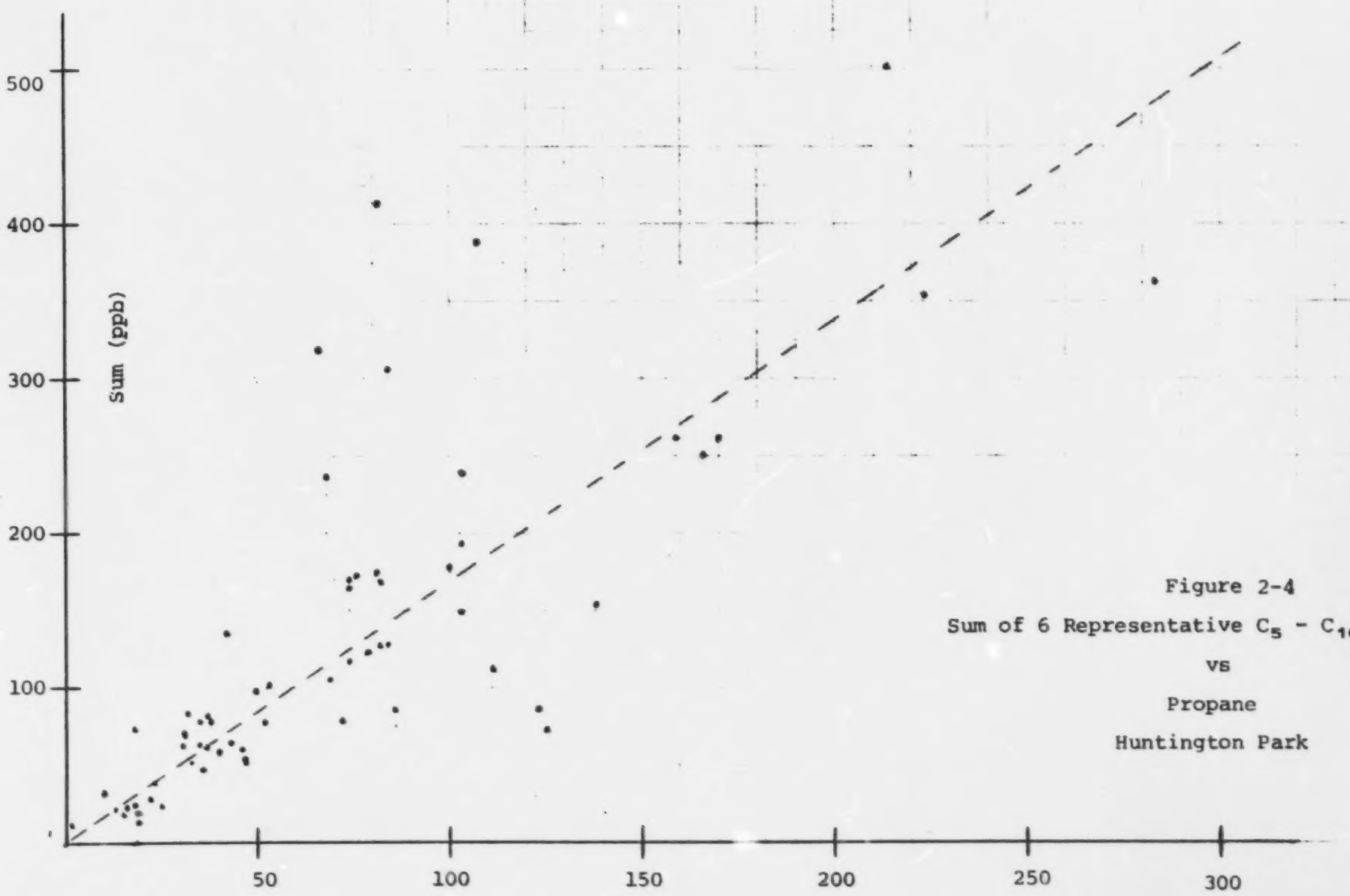


Figure 2-4

Sum of 6 Representative C_5 - C_{10} Hydrocarbons

vs

Propane

Huntington Park

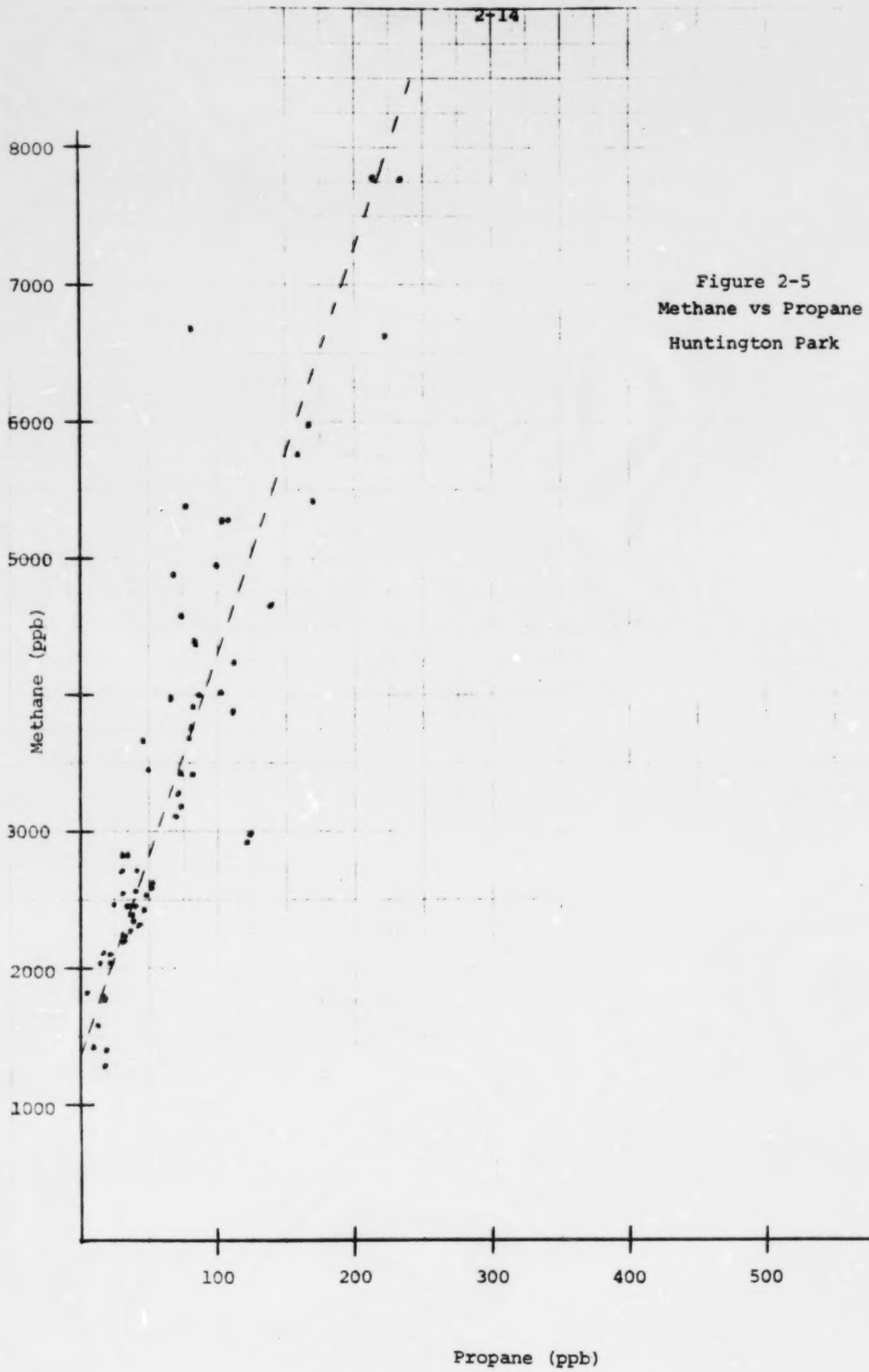
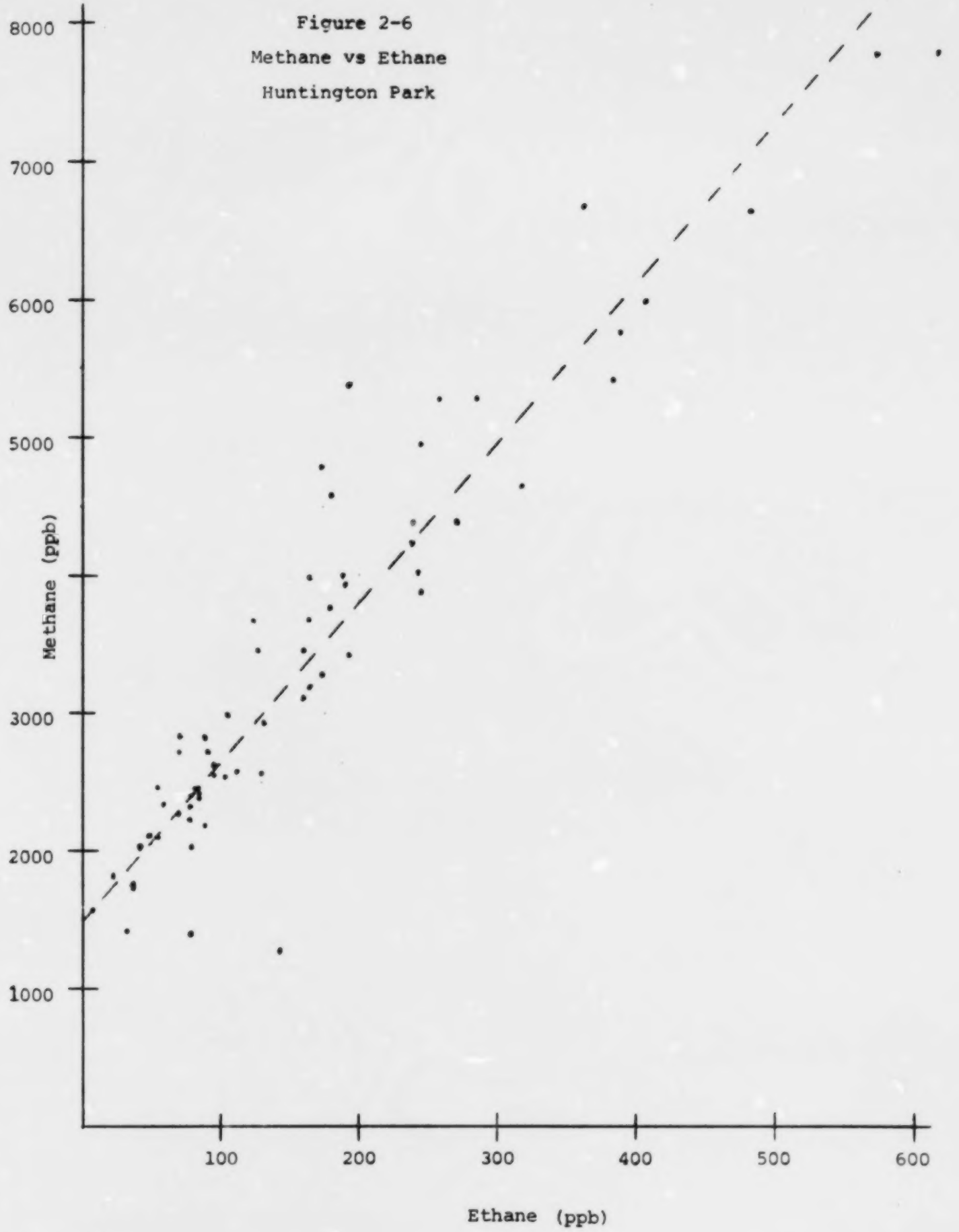


Figure 2-5
Methane vs Propane
Huntington Park

Figure 2-6
Methane vs Ethane
Huntington Park



this problem.

The low concentrations of fuel range olefins found in early morning samples taken before photochemical reactions were initiated by solar radiation are difficult to explain. Samples of gasolines in use during the test period were analyzed for individual hydrocarbons as part of a separate CRC program. The average olefin content reported by the seven participating laboratories was 7.3 wt.%, nearly 90% of which was made up of C_5 and C_6 hydrocarbons. The concentration of 2-methyl-2-butene reported was 1.1 wt.% for both premium and regular fuel. The concentrations of isopentane and n-pentane based on 65% premium and 35% regular fuel were 7.6% and 4.9% respectively. The measured isopentane to n-pentane ratio of 1.7 was close to that calculated from the fuel analyses. The expected 2-methyl-2-butene to n-pentane ratio was 0.22, but the actual early morning ratios found ranged from 0.08 to 0.12. Other fuel range olefins were also found in much lower concentrations than anticipated. Several possible explanations for this are: 1. Internally bonded fuel range olefins are present in exhaust at lower relative concentrations compared to the fuel than are saturates, 2. Internally bonded olefins react to a significant degree in the absence of ultraviolet radiation and photochemical reactions, 3. There is a significant source of C_5 saturates which contains little or no C_5 olefins. In any event the concentrations of fuel range olefins present at the start of photochemical activity were considerably less than expected. The importance of this finding is shown in subsequent sections which deal with chemical reaction rates.

NITROGEN OXIDES

Both nitric oxide and nitrogen dioxide are of major importance to

the photochemical reactions in the atmosphere of the Los Angeles Basin. These nitrogen oxides are produced in all combustion processes both vehicular and industrial. In most cases the portion emitted as nitric oxide is in excess of 90%. The data for Huntington Park show that the nitric oxide represented up to 80% of the total nitrogen oxides in samples collected before sunrise.

The ratio of carbon monoxide to nitrogen oxides is of interest in estimating source contributions and in determining the extent to which nitrogen oxides are lost from the atmosphere through reaction. The correlation found between carbon monoxide and total nitrogen oxides, nitric oxide, and nitrogen dioxide for 73 Huntington Park data points before 0900 PST along with the corresponding correlation coefficients and standard errors of estimate were:

	Correlation Coefficient	Standard Error of Estimate
CO (ppm) = 37.7 NO_x (ppm) - 1.43	0.80	3.81 ppm
CO (ppm) = 39.4 NO (ppm) + 1.86	0.74	4.32 ppm
CO (ppm) = 51.7 NO_2 (ppm) + 3.30	0.41	5.83 ppm

The poor correlation and high standard error of estimate indicate that at the time photochemical reactions are just starting, the ratio between carbon monoxide and nitrogen oxides is subject to wide variation.

Another factor to be studied is the variation in CO/NO_x ratio with time of day. Hourly averages for the carbon monoxide to nitrogen oxides ratio for 194 Huntington Park data points are plotted in Figure 2-7. It can be seen that the ratio passed through a minimum around 0830 PST. This was caused by the morning nitrogen oxides peak occurring consistently later than the carbon monoxide peak. The cause is not readily apparent. Changes in the

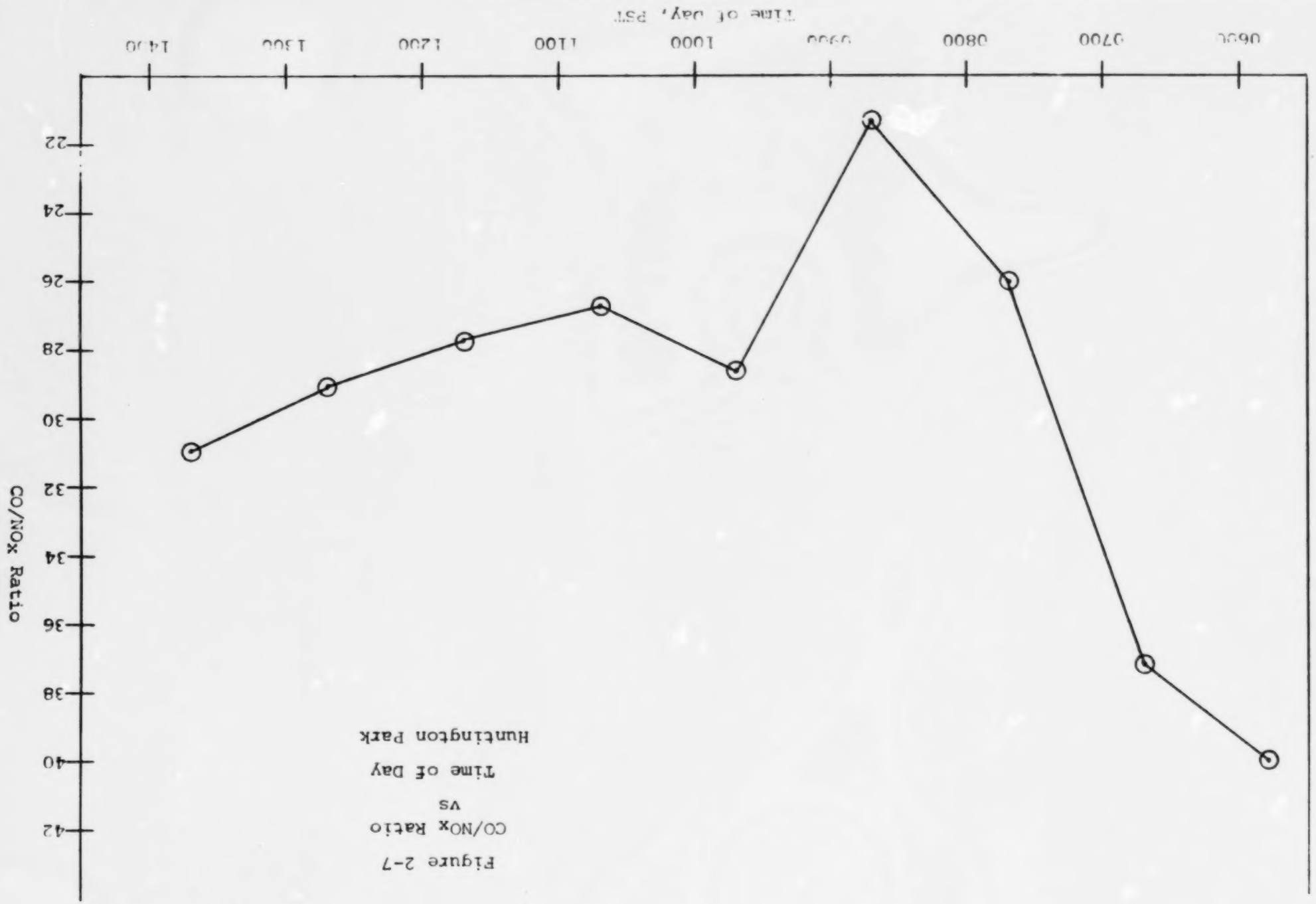


Figure 2-7

CO/NO_x Ratio

vs

Time of Day

Huntington Park

CO/NO_x ratio in auto exhaust as driving patterns change during the morning rush hour is a possible cause. However, the day to day variations in ratio for each time period were considerably greater than the time variations within day. This suggests that multiple sources are the primary cause of the poor correlation between carbon monoxide and nitrogen oxides. The relatively constant ratio from 1000 PST through 1330 PST is in strong disagreement with laboratory chamber studies where the nitrogen oxides are rapidly depleted as photochemical reactions proceed. A possible explanation is that loss of nitrogen oxides through atmospheric reactions is substantially slower than in laboratory systems and/or secondary sources emitting no carbon monoxide replace the nitrogen oxides as rapidly as they are removed by reaction.

The average carbon monoxide to nitrogen oxides ratio for the 194 points above was approximately 30. The accuracy of carbon monoxide concentrations below 5 ppm was not as good as at higher values because of the zero drift experienced with the non-dispersive infrared analyzer. In order to verify the validity of the overall average ratio, those data points where the carbon monoxide was equal to or greater than 5 ppm and the nitrogen oxides were equal to or greater than 15 pphm were studied. The distribution of the 58 points meeting these criteria was skewed to the high side so the median was determined rather than the mean. The median ratio was 32 with 70% of the 58 ratios between 20 and 40. Thus, part of the scatter in the 194 data points was due to poor accuracy at low concentrations. However the average was not distorted.

The carbon monoxide to nitrogen oxides ratio for exhaust from uncontrolled (pre-1966) cars was found to be 30 based on road tests at an average route speed of 25 miles per hour in urban areas[6]. The growing population

of device equipped cars, which emit substantially less carbon monoxide but at least as much nitrogen oxides as uncontrolled cars, would be expected to lead to a ratio lower than 30. Stationary source emissions, which are believed to contain more nitrogen oxides than carbon monoxide, should also reduce the atmospheric carbon monoxide to nitrogen oxides ratio.

The fact that the observed ratio was higher than expected might be explained by a loss of nitrogen oxides through chemical reaction, however the ratio did not decrease during the middle of the day when chemical reaction rates were greatest. It is more likely that area driving patterns resulted in lower vehicular nitrogen oxides emissions than the 25 mile per hour road test. The average carbon monoxide to nitrogen oxides ratio found for both the Commerce and El Monte sites in the 1969 survey was between 20 and 25. This ratio appears to reflect the influence of vehicles with carbon monoxide controls.

ALDEHYDES

Aldehydes are emitted by both vehicular and stationary sources, and they are also products of photochemical reactions. Data for formaldehyde, acrolein and total aliphatic aldehydes were collected in the field program.

The relationships among these three parameters were investigated by linear regression analysis. The results for 179 data points at Huntington Park were:

	Correlation Coefficient	Standard Error of Estimate
Form (pphm) = 0.67 Tot Ald (pphm) - 0.19	0.88	1.02 pphm
Form (pphm) = 2.57 Acr (pphm) + 1.99	0.40	1.98 pphm

The poor correlation with acrolein appears to result from the limited accuracy

of the data at the very low levels normally present. The formaldehyde to acrolein ratio approached 10 at the more reliable higher concentrations.

Attempts to correlate aldehydes with carbon monoxide and nitrogen oxides during various time periods proved fruitless as the correlation never exceeded 0.50. Aldehydes seemed to vary independently of other contaminants even before photochemical reactions were initiated.

The average and maximum concentrations of various aldehydes found at the two sites were:

	Concentration (pphm)			
	Huntington Park		El Monte	
	Max	Ave	Max	Ave
Aliphatic Aldehydes	17.3	4.5	14.8	5.1
Formaldehyde	13.6	2.8	9.0	2.5
Acrolein	1.0	0.3	0.8	0.2

2.3 FORMATION RATE OF NITROGEN DIOXIDE

BACKGROUND

The rate at which nitric oxide is converted to nitrogen dioxide is of great importance not only because the nitrogen dioxide formed is in itself objectionable, but to a greater extent because other noxious smog products such as ozone and peroxyacyl nitrates are formed only after most of the nitric oxide has been converted to nitrogen dioxide.

While some of the nitrogen dioxide present in the atmosphere is emitted as such from its source or is formed by the thermal reaction of nitric oxide and oxygen, the major portion present during smog episodes is

produced by photochemical reactions involving hydrocarbons, nitric oxide, nitrogen dioxide and ultraviolet radiation. Laboratory experiments have shown that the initial nitric oxide conversion rate is dependent on the concentration and reactivity of the hydrocarbons, the concentrations of nitric oxide and nitrogen dioxide, the ratio of hydrocarbon to nitrogen oxides, ultraviolet radiation intensity, temperature and humidity. Attempting to derive an expression relating the rate to all of these parameters in an initial step appeared unwise because their effects, except for ultraviolet radiation, have been shown to be non-linear[8]. Therefore, each parameter was treated separately.

ATMOSPHERIC RATES OF NO_2 FORMATION

The study of NO_2 formation rates from the data collected in the 1968 field survey was limited by the number of data points available for nitrogen oxides concentrations and ultraviolet radiation intensity. Failure to obtain delivery of the continuous nitric oxide - nitrogen dioxide instrument left only hourly readings from manual analyses for these two contaminants, while the availability of only one ultraviolet instrument for the ground sites reduced the number of data points recorded for radiation intensity.

Analyses at the Huntington Park site were made from 0530 PST until early afternoon, and thus completely covered the 0700 to 0930 period during which the bulk of the photochemical conversion of nitric oxide to nitrogen dioxide occurred. The El Monte site data was less useful because the conversion was usually well under way before the first analysis in the morning was made. The atmospheric formation rates of nitrogen dioxide were calculated from the differences between successive hourly measurements of nitric oxide and nitrogen dioxide. In making the calculation it was assumed

that the change in rate between the two successive points was linear and that the total nitrogen oxides changed only by atmospheric dilution. These assumptions were necessary because of the limited number of data points available and the lack of data for system input rates, dispersion rates and reaction rates for atmospheric nitrates. The relatively small variation with time noted for the CO/NO_x ratio in Section 2.2 of this report appears to validate the assumption that atmospheric dilution was the major cause of the variations in total nitrogen oxides concentration.

The average observed rate of nitrogen dioxide formation at Huntington Park was 0.7 ppb/min. The rates ranged from <0.5 ppb/min on low pollution days to a maximum of 2.2 ppb/min.

EFFECT OF NITRIC OXIDE CONCENTRATION

A regression analysis of nitrogen dioxide formation rate and nitric oxide concentration employing 46 data points from Huntington Park gave the following expression for the rate given in ppb/min.

$$\frac{d(NO_2)}{dt} = 9.59 \times 10^{-4} \ (NO)^{1.35}$$

Correlation Coefficient = 0.77

Standard Error of Estimate = 0.96 ppb min^{-1}

Standard Error of Correl. Coeff. = 0.17

The NO coefficient of 1.35 was higher than the values found for most hydrocarbons in laboratory studies at Scott[7] and General Motors Research[8]. Typical laboratory values for the nitric oxide concentration range found in the atmosphere included 0.4 for propylene, 0.6 for mesitylene and 0.3 for n-hexane. The correlation coefficient is not especially high but the standard error of the nitric oxide coefficient was only 0.17, so a

considerable difference between laboratory and atmospheric systems is indicated.

This relationship is useful in determining the value of controlling oxides of nitrogen emissions from motor vehicles and other sources. Unfortunately, no additional evidence can be gained from the 1968 data alone. A study of other factors which may have influenced the observed relationship points out the additional information required to reach a firmer conclusion. The addition of fresh emissions to the atmosphere has a greater effect on days when atmospheric concentrations are low. The emission rates are relatively constant from day to day (excluding weekends) while the dispersion rates vary considerably because of varying meteorological conditions. This means that the air near ground level will contain a greater proportion of fresh emissions on low concentration days. Since the major sources of nitrogen oxides emissions contain a much higher proportion (80 to 95%) of nitric oxide than nitrogen dioxide, the addition of these emissions can greatly reduce the observed apparent rate of nitrogen dioxide formation. This effect is greatest late in the conversion period when the contaminant concentrations are almost always lower than at the start of conversion and the disparity between the relative amounts of nitric oxide in the system inputs and the atmosphere is greatest.

An apparent negative conversion rate was noted on several occasions which illustrated the effect of unusual amounts of new emissions being added to the system. On October 16 the nitrogen dioxide decreased substantially and the nitric oxide increased from 0900 to 1005 PST. The analyst, noting this unexpected occurrence, went outdoors and found that a large slow-moving truck was being used to paint lines on the adjacent street. On another occasion when a negative rate was noted, spikes were found on the carbon

monoxide trace during the sampling period, suggesting that a vehicle had been left running near the sampling point.

Other factors which changed with time, such as hydrocarbon reactivity and ultraviolet irradiation, must also be examined to determine their effect at times when the nitric oxide concentration tended to be high as opposed to when it was low. This should be possible using the data obtained in the 1969 survey.

EFFECT OF HYDROCARBON CONCENTRATION AND REACTIVITY

The rates at which nitric oxide is converted to nitrogen dioxide in the presence of a large number of individual hydrocarbons have been determined by Glasson and Tuesday[9]. Each hydrocarbon was irradiated at 1 ppm with 0.38 ppm nitric oxide and 0.02 ppm nitrogen dioxide. The initial rates of nitrogen dioxide formation were computed from the time required to convert half of the nitric oxide to nitrogen dioxide. Additional experiments involving the irradiation of three gasolines under the same conditions showed that good agreement was obtained between the measured conversion rate and that calculated from the sum of the products of the mole fraction of each individual hydrocarbon multiplied by its rate of conversion as found in the previous tests with single hydrocarbons.

The same type of calculation used by Glasson and Tuesday was applied to a number of analyses for individual C_1 to C_{10} hydrocarbons made during the 0700 to 0930 PST period, and the results were compared to observed rates of nitrogen dioxide formation. The rate of nitrogen dioxide formation caused by each hydrocarbon was calculated as the product of its concentration (ppm) mulfiplied by the assigned nitrogen dioxide formation rate (ppb NO_2/min/ppm hydrocarbon). Some hydrocarbons were grouped into classes having similar

reactivities to expedite the calculation. The average rates for each class were calculated from the average molar reactivities for that class in the three gasolines employed by Glasson and Tuesday. The gasoline compositions were compared to other published data and the distribution within each class was found to be typical. Methane and acetylene were assigned zero reactivity rates. The atmospheric data for terminal butenes was not reliable because of baseline shifts in the chromatograms, so a figure of one-half the propylene concentration was assigned, based on exhaust data reported by Papa[10] and atmospheric data reported by Stephens[5] and Gordon et al[3].

The chromatographic peaks for some of the fuel range olefins were obscured by the much larger saturate peaks. In addition, some peak areas were below the minimum level counted by the integrator. For this reason the olefins clearly separated were calculated manually by direct measurement of the chromatograms, and the total found in this manner was adjusted for those olefins which were obscured by the saturates. The correction was based on published fuel analyses. This calculation was considered valid because the major fuel range olefins, such as 2-methyl-2-butene and trans-2-pentene, were clearly separated.

The calculated nitrogen dioxide formation rates for nine days are shown in Table 2-1. The calculated rates are compared with observed values in Table 2-2. The two agree within a factor of 2. Differences can be attributed to effects of factors such as hydrocarbon to nitrogen oxides ratio and ultraviolet radiation intensity. This indicates that the atmospheric formation rate of nitrogen dioxide can be accounted for by photochemical reactions involving hydrocarbons, nitrogen oxides and ultraviolet radiation

Table 2-1

Nitrogen Dioxide Formation Rates
Calculated from Atmospheric Analyses

Compound or Class	Reactivity Factor* (ppb/min/ppm HC)	Oct. 17, 1968 0847 PST			Oct. 18, 1968 0830 PST			Oct. 21, 1968 0750 PST		
		Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate
Ethane	0.25	.050	.0125	2.6	.059	.0148	2.6	.242	.0605	5.1
Propane	0.39	.031	.0121	2.5	.038	.0148	2.6	.103	.0402	3.4
Isobutane	0.62	.014	.0087	1.8	.037	.0229	4.0	.030	.0186	1.6
n-Butane	0.75	.049	.0368	7.6	.043	.0323	5.6	.088	.0660	5.6
C_5 and Higher Sat.	0.93	.200	.1860	38.6	.193	.1795	31.3	.316	.2940	24.8
Total Saturates		.344	.2561	53.2	.370	.2643	46.1	.779	.4793	40.5
Ethylene	1.70	.0320	.0544	11.3	.0340	.0578	10.1	.0870	.1479	12.5
Propylene + t-Butenes	3.50	.0200	.0700	14.5	.0210	.0735	12.8	.0525	.1837	15.5
C_4 and Higher Olefins	8.90	.0016	.0142	3.0	.0058	.0516	9.0	.0123	.1094	9.2
Total Olefins		.0536	.1386	28.8	.0608	.1829	31.9	.1518	.4410	37.2
Benzene	0.33	.0089	.0029	0.6	.0085	.0028	0.5	.0187	.0062	0.5
Toluene	1.30	.0190	.0247	5.1	.0262	.0341	6.0	.0436	.0566	4.8
C_8 and Higher Arom.	2.50	.0237	.0593	12.3	.0357	.0893	15.6	.0807	.2018	17.0
Total Aromatics		.0516	.0869	18.0	.0704	.1262	22.0	.1430	.2646	22.3
Total		.4492	.4816	100.0	.5012	.5734	100.0	1.0738	1.1849	100.0

* From Glasson and Tuesday[9] for system with 1 ppm hydrocarbon, 0.38 ppm NO, 0.02 ppm NO_2

Table 2-1
Continued

Nitrogen Dioxide Formation Rates
Calculated from Atmospheric Analyses

Compound or Class	Reactivity Factor* (ppb/min/ppm HC)	Oct. 22, 1968 0800 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Oct. 23, 1968 0852 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Oct. 28, 1968 0735 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate
Ethane	0.25	.406	.1015	4.8	.572	.1430	5.7	.105	.0263	4.1
Propane	0.39	.166	.0647	3.1	.283	.1104	4.4	.125	.0488	7.6
Isobutane	0.62	.034	.0211	1.0	.062	.0385	1.5	.015	.0093	1.5
n-Butane	0.75	.165	.1237	5.9	.254	.1905	7.6	.072	.0446	7.0
C_5 and Higher Sat.	0.93	.561	.5225	24.8	.838	.7800	31.2	.159	.1479	23.1
Total Saturates		1.332	.8335	39.6	2.009	1.2624	50.5	.476	.2769	43.2
Ethylene	1.70	.1390	.2360	11.2	.1610	.2735	10.9	.0240	.0408	6.4
Propylene + t-Butenes	3.50	.0675	.2365	11.2	.0750	.2625	10.5	.0465	.1628	25.4
C_4 and Higher Olefins	8.90	.0413	.3680	17.5	.0147	.1308	5.2	.0033	.0294	4.6
Total Olefins		.2478	.8405	39.9	.2507	.6668	26.7	.0738	.2330	36.3
Benzene	0.33	.0321	.0106	0.5	.0501	.0165	0.7	.0111	.0037	0.6
Toluene	1.30	.0764	.0992	4.7	.1034	.1346	5.4	.0187	.0243	3.8
C_8 and Higher Arom.	2.50	.1292	.3230	15.3	.1674	.4185	16.8	.0414	.1035	16.1
Total Aromatics		.2377	.4328	20.5	.3209	.5696	22.8	.0712	.1315	20.5
Total		1.8175	2.1068	100.0	2.5806	2.4988	100.0	.6210	.6414	100.0

* From Glasson and Tuesday[9] for system with 1 ppm hydrocarbon, 0.38 ppm NO, 0.02 ppm NO_2

Table 2-1
Continued

Nitrogen Dioxide Formation Rates
Calculated from Atmospheric Analyses

Compound or Class	Reactivity Factor* (ppb/min/ppm HC)	Oct. 30, 1968 0847 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Nov. 5, 1968 0745 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Nov. 6, 1968 0850 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate
Ethane	0.25	.033	.0083	3.6	.180	.0450	3.4	.0950	.0238	5.1
Propane	0.39	.010	.0039	1.7	.074	.0289	2.2	.0310	.0121	2.6
Isobutane	0.62	.003	.0019	0.8	.031	.0192	1.5	.0080	.0050	1.1
n-Butane	0.75	.013	.0098	4.3	.087	.0653	5.0	.0410	.0307	6.6
C_5 and Higher Sat.	0.93	.078	.0725	31.5	.337	.3135	23.9	.1477	.1372	29.4
Total Saturates		.137	.0964	41.9	.709	.4719	35.9	.3227	.2088	44.8
Ethylene	1.70	.0040	.0068	3.0	.1240	.2110	16.1	.029	.0493	10.6
Propylene + t-Butenes	3.50	.0165	.0578	25.1	.0660	.2310	17.6	.024	.0840	18.0
C_4 and Higher Olefins	8.90	.0000	.0000	0.0	.0117	.1042	7.9	.000	.0000	0.0
Total Olefins		.0205	.0646	28.1	.2017	.5462	41.6	.053	.1333	28.6
Benzene	0.33	.0021	.0007	0.3	.0193	.0064	0.5	.0062	.0020	0.4
Toluene	1.30	.0081	.0105	4.6	.0421	.0547	4.2	.0217	.0282	6.0
C_8 and Higher Arom.	2.50	.0232	.0580	25.2	.0936	.2340	17.8	.0377	.0943	20.2
Total Aromatics		.0334	.0692	30.1	.1550.	.2951	22.5	.0656	.1245	26.7
Total		.1909	.2302	100.0	1.0657	1.3132	100.0	.4413	.4666	100.0

* From Glasson and Tuesday[9] for system with 1 ppm hydrocarbon, 0.38 ppm NO, 0.02 ppm NO_2

Table 2-2

Calculated and Observed Nitrogen Dioxide Formation Rates at Huntington Park

Date	Sample Time (PST)	NO_2 Formation Rate Calculated (ppb min^{-1})	NO_2 Formation Rate Observed (ppb min^{-1})	Total Reactive Hydrocarbons (ppm)	Total Nitrogen Oxides (ppm)	Ratio HC/NO_x
Oct. 17	0847	0.48	0.9	0.45	0.22	2.0
Oct. 18	0830	0.57	1.1	0.50	0.24	2.1
Oct. 21	0750	1.18	0.6	1.07	0.23	4.6
Oct. 22	0800	2.11	1.0	1.82	0.30	6.1
Oct. 23	0852	2.50	1.6	2.58	0.51	5.1
Oct. 28	0735	0.64	0.6	0.62	0.20	3.1
Oct. 30	0847	0.23	<0.2	0.19	0.07	2.7
Nov. 5	0745	1.31	0.8	1.07	0.42	2.6
Nov. 6	0850	0.47	0.7	0.44	0.23	1.9

at the levels present in the atmosphere. This does not rule out the possibility that other mechanisms may contribute to nitrogen dioxide formation, but it limits them to a minor role.

The relative contribution of each hydrocarbon class to nitrogen dioxide formation as determined from the fraction it contributed to the calculated nitrogen dioxide formation rate is most interesting. Table 2-1 shows that the fuel range olefins accounted for 0 to 20% of the total. Calculations of additional chromatograms, including those given in Table 2-4, showed that these olefins contributed from 15 to 20% at the start of photochemical nitric oxide conversion (0700 PST) and from 0 to 5% at the time nitric oxide conversion was nearly complete and ozone formation began. The cracked olefins (ethylene, propylene and terminal butenes) contributed approximately 25% throughout the period. The aromatics contributed 20 to 25% and the saturates 40 to 50%.

The proportions of the calculated nitrogen dioxide formation rate assigned to each class in Table 2-1 are substantially different than those calculated using most reactivity scales. This difference is caused by the fact that in using the reactivity scales, it is assumed that reactivity based on initial reaction rates is applicable to the entire reaction period. In reality the very reactive hydrocarbons disappear rapidly as they are consumed in the reactions so that their contribution likewise decreases. On the other hand, the less reactive hydrocarbons disappear slowly and their overall reactivity remains relatively constant throughout the reaction period. A more realistic reactivity scale would be based on the average rate over the entire atmospheric reaction period (at least several hours) and not just the initial rate which may be valid for only the first 15 to 30 minutes of reaction.

EFFECT OF HYDROCARBON TO NITROGEN OXIDES RATIO

The work of Glasson and Tuesday[8] showed that increasing the hydrocarbon to nitrogen oxide ratio by increasing the hydrocarbon concentration above 1 ppm while holding the nitric oxide constant at 0.38 ppm always resulted in an increased nitrogen dioxide formation rate, but the percent increase in the rate was less than the percent increase in hydrocarbon. This slow rate increase was most noticeable for saturates and aromatics. Increasing hexane from 1 to 5 ppm increased the rate by 73%, and increasing o-xylene from 1 to 5 ppm increased the rate by 62%. A similar 400% increase in propylene increased the rate by 200%. Decreasing the ratio by lowering the hydrocarbon concentrations by 50% (from 1.0 to 0.5 ppm) resulted in a formation rate decrease of 31% for hexane, 31% for o-xylene and 40% for propylene. The results obtained by changing the hydrocarbon to nitrogen oxides ratio by varying the nitric oxide and keeping the hydrocarbon concentration at 1 ppm showed similar trends.

These laboratory results demonstrate that the nitrogen dioxide formation rate increases as the ratio is increased but the rate change is proportionately much less than the ratio change. In other words, Rate = $k \times Ratio^n$ where n is approximately 0.4 for hexane and o-xylene and 0.7 for propylene. Limited data indicated that changing the reactant concentrations while keeping the ratio constant also resulted in a rate change proportionately slower than the change in concentration. For propylene the relationship was Rate = $k \times Concentration^{0.86}$ and for mesitylene it was Rate = $k \times Concentration^{0.7}$. This means that theoretically the reactivity factors used to calculate the nitrogen dioxide formation rate are applicable only at a total hydrocarbon concentration of 1 ppm and that they are less when the hydrocarbon is greater than 1 ppm and vice versa.

The atmospheric data shown in Table 2-2 agree with the laboratory findings in that the calculations predict a higher rate than observed at high ratios (4.6 to 6.1) and predict a lower rate than observed at low ratios 1.9 to 2.1). The effect of total concentration on molar reactivity is difficult to separate from the ratio effect. Effects due to other parameters, e.g. radiation intensity and temperature, are responsible for part of the differences between the calculated and observed rates. These, however, cannot account for the magnitude of the ratio effects noted.

Although there are not enough data points to validate the conclusions statistically, there is strong evidence that hydrocarbon - nitrogen oxide ratios play a similar role in the atmosphere as in laboratory systems.

EFFECT OF ULTRAVIOLET RADIATION INTENSITY

Laboratory experiments[8] have shown that the rate of nitrogen dioxide formation is directly proportional to radiation intensity for a number of hydrocarbons of different classes. Attempts to verify this by multiple regression analyses of 46 data points from Huntington Park, substituting the ultraviolet measurements at El Monte for the points at which there were no data at Huntington Park, resulted in a regression coefficient of 0.25 and a correlation coefficient of -0.13. The complete lack of correlation found does not necessarily mean that the laboratory relationship is not valid but rather that the day to day variations in nitrogen dioxide formation rate were primarily caused by changes in contaminant concentration and ratio, and these parameters exhibited greater day to day variation than did radiation intensity. However, it was quite apparent that nitrogen dioxide formation was delayed on days where fog persisted to mid-morning and greatly reduced on cloudy days.

EFFECTS OF TEMPERATURE AND HUMIDITY

Temperature is known to increase the rates of certain reactions involved in the conversion of nitric oxide to nitrogen dioxide and thereby increase the overall rate. The effect of humidity is subject to debate. While some investigators have reported that low humidity leads to decreased nitrogen dioxide formation rates, others have employed dry systems without effect. Humidity effects were noted at Scott[7] after prolonged use of a dry system in the study of less reactive hydrocarbons. The effects were believed due to reactions on the chamber wall because they were noted only after dry gas had been passed through the chamber for several days.

It was difficulat to assess the effect of temperature on the atmospheric nitrogen dioxide formation rate because the temperature during the conversion period changed little from day to day. There were three days in October 1968 on which the temperature was substantially above normal. Data for two of these, October 17 and 18, are compared to data for three other days in Table 2-3. All data were adjusted to 0830 PST, the approximate mid-point of the conversion period. November 6 offers the best comparison because the concentrations and ratios were nearly identical to those on October 17 and 18. The rate on November 6 is approximately 40% lower than on both October 17 and 18, but part of this can be accounted for by a 20% reduction in radiation intensity. The lower rates on October 21 and 22 are partially due to the ratio effects discussed previously. These comparisons suggest that temperature has a small but real effect on the nitrogen dioxide formation rate, but there is no evidence that lower humidity reduces the rate.

Table 2-3

Calculated and Observed Nitrogen Dioxide Formation Rates at Huntington Park at 0830 PST

Date	NO_2 Formation Rate: Calculated (ppb min^{-1})	NO_2 Formation Rate: Observed (ppb min^{-1})	Temp. (^{o}F)	Relative Humidity (%)	Ratio HC/NO_x
Oct. 17	0.61	1.1	74	18	2.1
Oct. 18	0.57	1.1	74	15	2.1
Oct. 21	1.01	0.7	57	92	3.7
Oct. 22	1.99	0.9	60	70	5.6
Nov. 6	0.59	0.7	58	74	2.1

2.4 FORMATION OF OZONE AND OXIDANT

BACKGROUND

Ozone and other oxidants begin to accumulate in the atmosphere after most of the nitric oxide has been converted to nitrogen dioxide. The term oxidant is used to refer to any compound which will generate iodine when passed through a buffered potassium iodide solution. Ozone reacts rapidly with the iodide ion so that its full concentration is recorded. On the other hand, compounds such as nitrogen dioxide react more slowly and less completely so that their response is much less than unity. Since the time from absorption of the compound until the measurement is made, whether by colorimetry or coulometry, varies from instrument to instrument, the response factors for oxidants other than ozone must be determined for each instrument or procedure. For example, nitrogen dioxide has a response factor of 0.08 with the Mast Ozone Recorder and up to twice that amount with the Beckman Acralyzer.

Nearly all laboratory studies have been concerned with the total oxidant present in the test chamber after an arbitrary irradiation period rather than the rate at which oxidant forms once the nitric oxide has been converted to nitrogen dioxide. The irradiation times have been shorter than the actual atmospheric reaction period, and serious losses of nitrogen dioxide have frequently occurred by the time oxidant began to form. These losses have been explained as due to nitric acid formation on the walls of the chamber. Therefore, laboratory oxidant formation data must be treated as qualitative rather than quantitative when making comparisons with the atmospheric system.

The atmospheric reactions which convert oxygen to ozone are believed to be analogous to those which convert nitric oxide to nitrogen dioxide. Thus, it was hypothesized that the parameters and hydrocarbon reactivities used in studying nitrogen dioxide formation should also be applicable to ozone and oxidant formation.

Continuous data for ozone and oxidant were available for both sites. Ozone was determined by difference between total oxidant and oxidant after removing the ozone by trans-2-butene reaction according to the procedure developed by Buffalini[11]. The rates of formation of ozone and oxidant were read from the slope of the recorder chart. This was found to yield more precise rates than use of the half hour averages.

EFFECT OF REACTANT CONCENTRATIONS AND HYDROCARBON REACTIVITY

The calculated nitrogen dioxide formation rates of samples analyzed just before the onset of ozone formation or during the first hour after its onset for nine separate days are shown in Table 2-4. The calculations were made in the same manner as those in Section 2.3. The mean contribution by classes for the nine samples was: saturates, 54%; aromatics, 26%; cracked olefins, 19%; and fuel range olefins, 1%. Nearly all of the fuel range olefins were consumed in nitrogen dioxide formation and thus not available to produce ozone.

The calculated nitrogen dioxide formation rates along with the observed rates of oxidant formation, total reactive hydrocarbons, nitrogen oxides and hydrocarbon to nitrogen oxides ratios for the nine days are summarized in Table 2-5. On the three days for which the samples illustrated were collected before the start of ozone formation, the results have been interpolated to one-half hour after ozone was first noted. This permits a

Table 2-4

Nitrogen Dioxide Formation Rates
Calculated from Atmospheric Analyses

Compound or Class	Reactivity Factor* (ppb/min/ppm HC)	Oct. 21, 1968 1019 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Oct. 22, 1968 0956 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Oct. 23, 1968 1035 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate
Ethane	0.25	.160	.0400	5.7	.324	.0810	4.9	.164	.0410	4.4
Propane	0.39	.069	.0269	3.8	.141	.0550	3.3	.074	.0289	3.1
Isobutane	0.62	.016	.0099	1.4	.031	.0192	1.2	.018	.0112	1.2
n-Butane	0.75	.069	.0518	7.4	.181	.1357	8.2	.100	.0750	8.1
C_5 and Higher Sat.	0.93	.246	.2290	32.6	.639	.5940	35.8	.358	.3330	35.9
Total Saturates		.560	.3576	50.9	1.316	.8849	53.3	.714	.4891	52.7
Ethylene	1.70	.042	.0714	10.2	.1060	.1802	10.9	.0570	.0968	10.4
Propylene + t-Butenes	3.50	.027	.0945	13.5	.0465	.1628	9.8	.0315	.1103	11.9
C_4 and Higher Olefins	8.90	.001	.0089	1.3	.0019	.0169	1.0	.0000	.0000	0.0
Total Olefins		.070	.1748	24.9	.1544	.3599	21.7	.0885	.2071	22.3
Benzene	0.33	.0137	.0045	0.6	.0386	.127	0.8	.0110	.0036	0.4
Toluene	1.30	.0347	.0451	6.4	.0931	.1210	7.3	.0572	.0774	8.0
C_8 and Higher Arom.	2.50	.0480	.1200	17.1	.1127	.2818	17.0	.0617	.1543	16.6
Total Aromatics		.0964	.1696	24.2	.2444	.4155	25.0	.1299	.2323	25.0
Total		.7264	.7020	100.0	1.7148	1.6603	100.0	.9324	.9285	100.0

From Glasson and Tuesday[9] for system with 1 ppm hydrocarbon, 0.38 ppm NO, 0.02 ppm NO_2

Table 2-4
Continued

Nitrogen Dioxide Formation Rates
Calculated from Atmospheric Analyses

Compound or Class	Reactivity Factor* (ppb/min/ppm HC)	Oct. 24, 1968 1015 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Oct. 25, 1968 1004 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Oct. 26, 1968 1110 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate
Ethane	0.25	.049	.0123	3.4	.180	.0450	4.1	.160	.0400	5.4
Propane	0.39	.018	.0070	1.9	.081	.0316	2.9	.074	.0289	3.9
Isobutane	0.62	.006	.0037	1.0	.023	.0143	1.3	.016	.0099	1.3
n-Butane	0.75	.044	.0330	9.1	.105	.0787	7.2	.084	.0630	8.5
C_5 and Higher Sat.	0.93	.168	.1560	42.9	.388	.3610	33.1	.292	.2715	36.8
Total Saturates		.285	.2120	58.3	.697	.5306	48.7	.626	.4133	56.0
Ethylene	1.70	.008	.0136	3.7	.0760	.1292	11.9	.0490	.0833	11.3
Propylene + t-Butenes	3.50	.009	.0315	8.7	.0375	.1313	12.1	.0180	.0630	8.5
C_4 and Higher Olefins	8.90	.000	.0000	0.0	.0060	.0534	4.9	.0010	.0089	1.2
Total Olefins		.017	.0451	12.4	.1195	.3139	28.8	.0680	.1552	21.0
Benzene	0.33	.0047	.0015	0.4	.0231	.0076	0.7	.0189	.0062	0.8
Toluene	1.30	.0300	.0390	10.7	.0464	.0602	5.5	.0387	.0503	6.8
C_8 and Higher Arom.	2.50	.0265	.0663	18.2	.0708	.1770	16.3	.0452	.1130	15.3
Total Aromatics		.0612	.1068	29.4	.1403	.2448	22.5	.1028	.1695	23.0
Total		.3632	.3639	100.0	.9568	1.0893	100.0	.7968	.7380	100.0

* From Glasson and Tuesday[9] for system with 1 ppm hydrocarbon, 0.38 ppm NO, 0.02 ppm NO_2

Table 2-4
Continued

Nitrogen Dioxide Formation Rates
Calculated from Atmospheric Analyses

Compound or Class	Reactivity Factor* (ppb/min/ppm HC)	Oct. 28, 1968 0955 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Oct. 31, 1968 1115 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate	Nov. 1, 1968 0950 PST Conc. (ppm)	Calculated Rate of NO_2 Formation (ppb/min)	% Total Rate
Ethane	0.25	.131	.0328	5.7	.0320	.0080	11.0	.0260	.0065	4.8
Propane	0.39	.123	.0480	8.3	.0110	.0430	5.9	.0100	.0039	2.9
Isobutane	0.62	.019	.0117	2.0	.0020	.0012	1.7	.0020	.0012	.9
n-Butane	0.75	.084	.0630	10.9	.0000	.0075	10.3	.0090	.0068	5.0
C_5 and Higher Sat.	0.93	.158	.1470	25.4	.0232	.0216	29.8	.0578	.0537	39.7
Total Saturates		.515	.3025	52.2	.0782	.0426	58.7	.1048	.0721	53.3
Ethylene	1.70	.036	.0612	10.6	.004	.0068	9.4	.004	.0068	5.0
Propylene + t-Butenes	3.50	.018	.0630	10.9	.002	.0070	9.6	.002	.0070	5.2
C_4 and Higher Olefins	8.90	.002	.0178	3.0	.000	.0000	0.0	.000	.0000	0.0
Total Olefins		.056	.1420	24.5	.006	.0138	19.0	.006	.0138	10.2
Benzene	0.33	.0155	.0051	.9	.0089	.0029	4.0	.0104	.0034	2.5
Toluene	1.30	.0319	.0415	7.2	.0033	.0043	5.9	.0089	.0116	8.6
C_8 and Higher Arom.	2.50	.0353	.0883	15.2	.0036	.0090	12.4	.0137	.0343	25.4
Total Aromatics		.0827	.1349	23.3	.0158	.0162	22.3	.0330	.0493	36.5
Total		.6537	.5794	100.0	.1000	.0726	100.0	.1438	.1352	100.0

* From Glasson and Tuesday[9] for system with 1 ppm hydrocarbon, 0.38 ppm NO, 0.02 ppm NO_2

Table 2-5

Calculated Nitrogen Dioxide Formation Rates
and Observed Oxidant Formation Rates at Huntington Park

Date	Sample Time (PST)	Calculated Rate of NO_2 Formation (ppb min^{-1})	Observed Rate of Oxidant Formation (ppb min^{-1})	Total Reactive Hydrocarbons (ppm)	Total Nitrogen Oxides (ppm)	Ratio HC/NO_x
Oct. 21*	1110	0.52	1.3	0.57	0.20	2.8
Oct. 22	0956	1.66	1.6	1.71	0.33	5.2
Oct. 23	1055	0.93	1.6	0.93	0.37	2.5
Oct. 24	1015	0.36	0.7	0.36	0.13	2.8
Oct. 25*	1110	0.69	1.7	0.65	0.23	2.8
Oct. 26	1110	0.74	1.8	0.80	--	--
Oct.28*	1210	0.57	1.0	0.65	0.17	3.8
Oct. 31	1115	0.07	0.0	0.10	0.05	2.0
Nov. 1	1030	0.14	0.2	0.14	0.06	2.3

* Values obtained by interpolation to the time indicated.

direct comparison between calculated and observed rates. The observed oxidant formation rates are approximately twice the calculated nitrogen dioxide rates except on October 22 where a high HC/NO_x ratio persisted throughout the day and on October 31 which was a cloudy day with low contaminant concentrations. Eight of the nine observed oxidant formation rates were within ±0.32 ppb min^{-1} of twice the calculated nitrogen dioxide rates. The oxidant rates also appeared to correlate well with nitrogen dioxide concentrations. Unfortunately, there were not enough days with high oxidant formation rates to derive a mathematical relationship.

EFFECT OF TEMPERATURE AND HUMIDITY

The data for the nine days listed in Table 2-5 are revised to include temperature, humidity and wind data in Table 2-6. There were no apparent effects of any of these parameters on oxidant rate.

ACCUMULATION OF OXIDANTS AND OZONE

The total amount of oxidant and ozone that accumulates in the atmosphere is of even greater interest than the initial rate at which it forms. In the case of nitrogen dioxide the maximum atmospheric concentration is limited by the total nitric oxide and nitrogen dioxide emitted to the atmosphere. However, there is no such constraint on ozone since it is formed from oxygen which is in abundant supply.

A study of the continuous strip chart records for oxidant and ozone showed that the initial rate of ozone formation could be decreased by only three factors. They were a decrease in contaminant concentration, a decrease in ultraviolet radiation, and an increase in the proportion of new emissions. When none of these occurred, ozone continued to accumulate to high levels. The reaction rate of ozone with other contaminants increases

Table 2-6

Oxidant Formation Rates at
Various Atmospheric Conditions

Sample Date	Time (PST)	Calculated Rate of NO_2 Formation (ppb min^{-1})	Observed Rate of Oxidant Formation (ppb min^{-1})	Temp (F^{o})	Relative Humidity (%)	Wind Speed (mph)	Wind Direction (Deg. True)
Oct. 21	1110	0.52	1.3	73	28	2	197
Oct. 22	0956	1.66	1.6	71	33	2	220
Oct. 23	1055	0.93	1.6	86	6	2	291
Oct. 24	1015	0.36	0.7	89	4	2	345
Oct. 25	1110	0.69	1.7	83	19	3	185
Oct. 26	1110	0.74	1.8	78	28	3	220
Oct. 28	1210	0.57	1.0	69	59	3	177
Oct. 31	1115	0.07	0.0	65	62	2	88
Nov. 1	1030	0.14	0.2	67	48	4	55

as the ozone increases so that eventually this becomes a controlling factor in limiting the ozone concentration, but this factor had no noticeable effect at either ground site.

This helps to explain the accumulation of high concentrations of ozone in remote ground sites and aloft. The amount of inhibition due to nitric oxide in fresh emissions is negligible at these points so that ozone continues to increase as long as the sun provides ultraviolet radiation. The rate of increase is limited by the low reactant concentrations, but the radiation period may be as long as 10 to 12 hours.

EQUILIBRIUM EXPRESSION FOR OZONE

The equilibrium relationship for ozone postulated by Stephens[12] is:

$$(O_3) = \frac{ka\,(UV)\,(NO_2)}{k_4\,(NO)}$$

The rates of the reactions involved in this equilibrium are so rapid that only a few seconds are required to regain equilibrium if one of the variables changes in magnitude. In order to facilitate testing the equation was solved for k:

$$k = \frac{(NO)\,(O_3)}{(UV)\,(NO_2)} \text{ where } k = \frac{ka}{k_4}$$

Calculations of k from Huntington Park and El Monte data (referring to the strip charts for ozone concentrations) for a number of high oxidant days are shown in Tables 2-7 and 2-8. When the values of k were plotted against the inverse of the absolute temperature in Figure 2-8, it was observed that the data points for the two sites belonged to the same population. The equilibrium expression appeared reasonably valid with k being temperature dependent. The value of k doubled for each $10^{\circ}F$ increase in temperature. This means that

Table 2-7 Ozone Equilibrium Data - Huntington Park

Date	Time (PST)	O_3 (pphm)	NO (pphm)	NO_2 (pphm)	UV (w/m^2)	K	Temp. (^oF)	T^{-1} ($^oR^{-1}$)
10/21	1145	9.0	1.3	8.4	20.7	0.0673	76.5	.001864
	1255	8.5	3.2	12.2	19.2	0.1161	76.0	.001866
	1358	6.5	1.3	11.2	13.3	0.0567	72.0	.001880
10/22	1115	11.0	2.6	19.5	21.15	0.0693	80	.001851
	1240	12.0	1.1	6.7	21.0	0.0938	80.5	.001850
10/23	1208	16.0	2.2	12.6	21.2	0.1318	90.5	.001816
	1330	8.8	0.6	7.8	16.8	0.0403	83.5	.001839
10/24	1250	13.0	0.9	5.2	19.65	0.1145	96	.001798
	1400	11.0	1.0	9.5	13.1	0.0884	92	.001811
10/25	1133	8.5	2.3	16.7	19.5	0.0600	85	.001834
	1245	12.0	6.8	6.0	15.25	0.8918	82	.001841
10/28	1200	4.5	1.3	15.7	18.2	0.0205	71	.001883
	1324	11.0	0.9	14.7	15.4	0.0437	75	.001883
11/6	1122	2.0	1.2	8.7	18.7	0.0148	71	.001883
	1233	4.0	1.5	8.7	16.8	0.0410	74.5	.001871

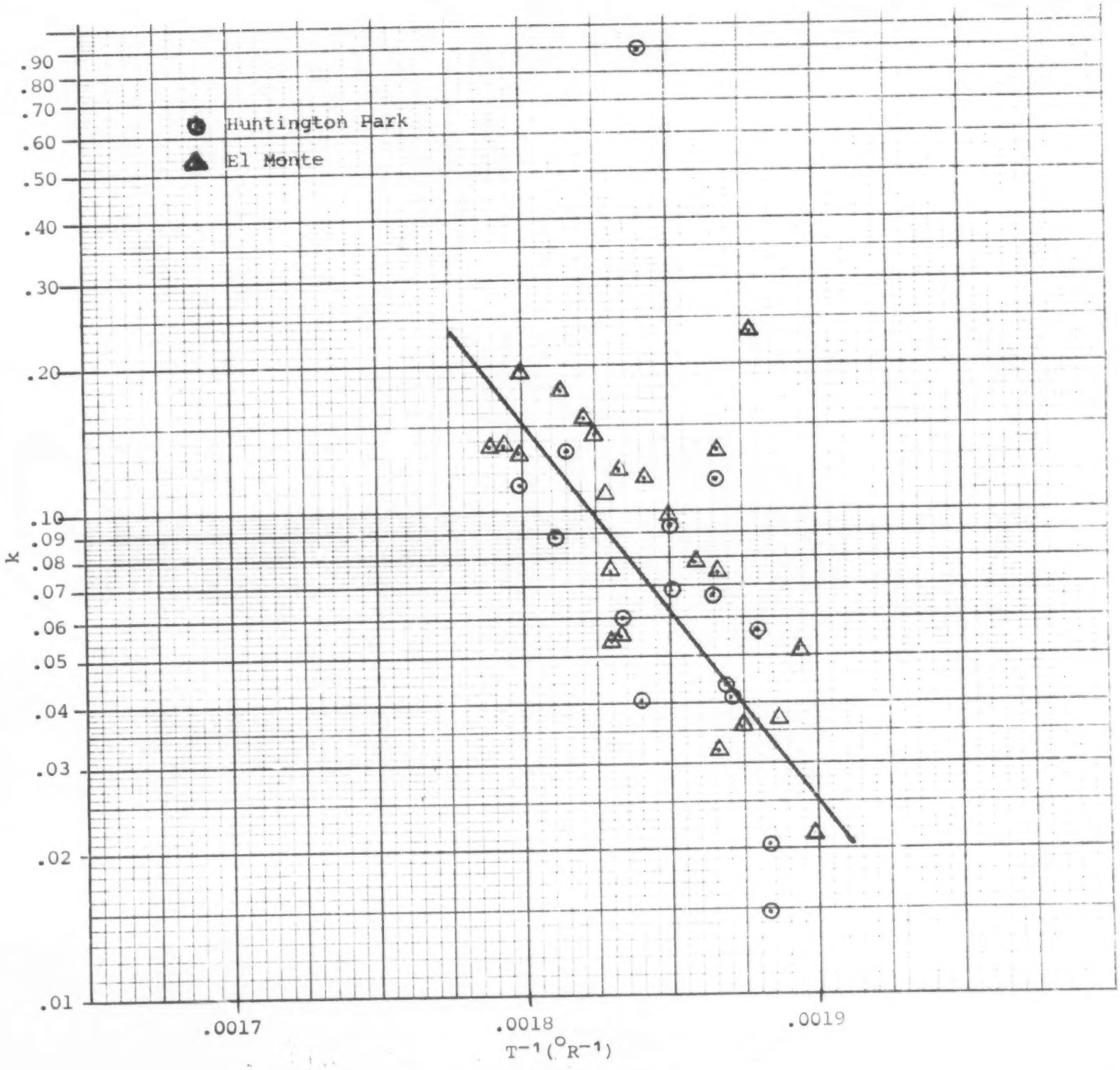
Table 2-8 Ozone Equilibrium Data - El Monte

Date	Time (PST)	O_3 (pphm)	NO (pphm)	NO_2 (pphm)	UV (w/m^2)	k	Temp. (^oF)	T^{-1} ($^oR^{-1}$)
10/10	1312	5.0	0.7	6.6	14.36	0.037	71	.001887
10/18	1400	8.8	0.9	10.0	6.7	0.118	84	.001842
10/21	1135	8.0	1.0	12.3	20.36	0.032	77	.001866
	1242	16.0	0.6	6.4	19.32	0.078	79	.001859
	1350	16.0	0.5	5.9	13.80	0.098	81.5	.001850
10/22	1134	10	1.6	13.8	21.5	0.054	87.5	.001830
	1235	22	1.1	14.2	22.7	0.075	87.5	.001830
	1338	30	0.8	10.4	21.4	0.108	88	.001828
	1442	20.5	0.4	6.9	21.6	0.055	86.5	.001833
10/23	1130	11.5	1.0	2.8	22.9	0.1793	92.5	.001813
	1235	12	0.9	2.7	20.14	0.1986	96.5	.001800
	1340	15.8	0.7	5.8	14.6	0.1306	97	.001799
	1445	24	0.5	11.8	8.4	0.1211	95.5	.001833
10/24	1328	9.5	0.7	3.0	16.2	0.1368	100	.001789
	1435	10	0.8	5.2	11.2	0.1374	98.5	.001794
10/25	1305	17	0.9	6.5	15.1	0.156	90	.001821
	1410	14	1.1	10.0	10.7	0.1439	89	.001825
10/28	1212	8	1.3	15.7	18.5	0.0358	74.5	.001874
	1315	14	1.1	13.0	15.9	0.0745	77	.001866
	1420	11	1.4	11.6	10.0	0.2319	73.5	.001878
10/29	1155	9.5	1.0	9.8	18.8	0.0516	69	.001894
	1303	6	0.6	10.4	16.1	0.0215	68	.001898

Figure 2-8 Ozone Equilibrium Constant (k) vs

Reciprocal of Absolute Temperature

$$k = \frac{(O_3)(NO)}{(UV)(NO_2)}$$



if the UV and NO_2/NO ratio remain constant, the ozone concentration will be twice as large at 90°F as at 80°F and four times as large at 100°F as at 80°F.

2.5 FORMATION OF ALDEHYDES

Various aldehydes and ketones are produced by photochemical reactions involving hydrocarbons and nitrogen oxides. Formaldehyde is formed in much greater quantities than other aldehydes. Laboratory studies have shown that the specific aldehydes emitted and the yield of each was a function of the hydrocarbon structure and the experimental conditions. The yield of formaldehyde per mole of hydrocarbon reacted varied over the range from less than 0.1 to 1.0. An assumed mean of 0.5 seems to be of the right order of magnitude. If it is further assumed that each mole of hydrocarbon which is consumed results in the conversion of two moles of nitric oxide to nitrogen dioxide[13], the estimated rate of formaldehyde formation would be one-fourth of the rate of nitrogen dioxide formation.

It is difficult to determine precise formation rates of formaldehyde from the 1968 data because of the low concentrations and contributions from non-photochemical sources. However, it appears valid to state that the rate was within a factor of 2 of the predicted rate. On days with a nitrogen dioxide formation rate of 6 to 10 pphm/hr the formaldehyde rate was approximately 2 pphm/hr. The formaldehyde rate also appears related to reactive hydrocarbon concentration. Higher rates were noted on days with high hydrocarbon - nitrogen oxide ratios as compared to low ratio days with a similar nitrogen dioxide formation rate. On days with a nitrogen dioxide formation rate of less than 4 pphm/hr the formaldehyde rate did not exceed 1 pphm/hr.

The rates of formation of total aliphatic aldehydes were in the same

range as for formaldehyde, but more erratic. This may be due to the accuracy of the determinations since there was no general diurnal pattern for the differences between total aldehydes and formaldehyde.

2.6 PHOTOCHEMICAL AGE OF THE ATMOSPHERE

For the purpose of this analysis the photochemical age of an air parcel will be defined as the average period of time that the reactive hydrocarbons in the parcel have participated in photochemical reactions. This knowledge is required to assess the relative contributions of individual hydrocarbons and specific sources of hydrocarbons to smog formation. The more reactive hydrocarbons contribute significantly during the initial period of photochemical activity, but they are consumed in the reactions and their importance diminishes with time. The less reactive hydrocarbons are present in higher concentrations and their relative contribution increases as the reaction time increases.

The extent to which hydrocarbons have reacted can be measured by use of ratios between reactive and unreactive hydrocarbons. Stephens[4] has used the propylene to acetylene ratio to demonstrate this with samples collected at Riverside and other locations. Unfortunately, this ratio is not always valid because of apparent additional sources of propylene which do not contain acetylene. The data from the Huntington Park site showed a modest decrease in propylene-acetylene ratio from 0.3 to 0.2 on high oxidant days, but no consistent change on other days even when the C_4 to C_6 terminal olefins with similar reactivities were substantially reduced. The 1967 data collected by NAPCA and the California ARB[3] show no change in propylene-acetylene ratio with time for either downtown Los Angeles or Azusa.

The chromatographic data for individual C_5 to C_{10} hydrocarbons was studied to find other ratios between reactive and relatively unreactive hydrocarbons which could be used to measure the extent of hydrocarbon reaction. The criteria were that the reactive compound disappeared at a significant rate yet measurable amounts remained at all times, while the unreactive compound disappeared much more slowly. The ratios between the two hydrocarbons during the early morning period before photochemical activity started must be the same from day to day. Visual examination of the data indicated that 1,2,4-trimethylbenzene (1,2,4-TMB) should be an ideal reactive hydrocarbon and that n-pentane, toluene and ethylbenzene were prime choices for the relatively unreactive hydrocarbon. The correlations obtained using 39 data points taken at Huntington Park before 0800 PST with the corresponding correlation coefficients and standard errors of estimate were:

	Correlation Coefficient	Standard Error of Estimate
1,2,4-TMB (ppb) = 0.339 n-pentane (ppb) + 0.08	0.917	3.76 ppb
1,2,4-TMB (ppb) = 0.206 toluene (ppb) + 1.62	0.908	3.94 ppb
1,2,4-TMB (ppb) = 1.55 ethylbenzene (ppb) - 0.59	0.959	2.67 ppb
1,2,4-TMB (ppb) = 0.128 (n-pentane + toluene + ethylbenzene (ppb) - 0.03	0.952	2.89 ppb

Ethylbenzene and the sum of n-pentane, toluene and ethylbenzene, which showed the best correlation, were used to measure the extent to which the 1,2,4-trimethylbenzene had reacted as the day proceeded.

Correlations of the ratios of 1,2,4-TMB to ethylbenzene and of 1,2,4-TMB to the sum of n-pentane, toluene and ethylbenzene with time after 0800 PST are summarized in Table 2-9. Correlation coefficients were higher

Table 2-9

Correlation of 1,2,4-Trimethylbenzene (1,2,4-TMB)
with Various Parameters

Data Source: 39 Hydrocarbon Analyses at Huntington Park before 0800 PST

Dependent Variable	Independent Variable(s)	Correlation Coefficient
1,2,4-TMB	n-Pentane	0.92
1,2,4-TMB	Toluene	0.91
1,2,4-TMB	Ethylbenzene(EtB)	0.96
1,2,4-TMB	Σ 3 HC above	0.95

Data Source: 52 Hydrocarbon Analyses at Huntington Park after 0800 PST

Dependent Variable	Independent Variable(s)	Correlation Coefficient
Time	1,2,4-TMB/EtB	-0.25
Time	1,2,4-TMB/Σ 3 HC	-0.52
Time	Oxidant	0.55
Time	1,2,4-TMB/EtB, Oxidant	0.58
Time	1,2,4-RMB/Σ 3 HC, Oxidant	0.64
Time	1,2,4-TMB/EtB, Oxidant, Σ 3 HC	0.69
Time	1,2,4-TMB/Σ 3 HC, Oxidant, Σ 3 HC	0.72

Data Source: 44 Hydrocarbon Analyses at Huntington Park between 0800 and 1300 PST

Dependent Variable	Independent Variable(s)	Correlation Coefficient
Time	1,2,4-TMB/EtB	-0.31
Time	1,2,4-TMB/Σ 3 HC	-0.61
Time	Oxidant	0.53
Time	1,2,4-TMB/EtB, Oxidant	0.57
Time	1,2,4-TMB/Σ 3 HC, Oxidant	0.68
Time	1,2,4-TMB/EtB, Oxidant Σ 3 HC	0.70
Time	1,2,4-TMB/Σ 3 HC, Oxidant, Σ HC	0.76

Data Source: 32 Hydrocarbon Analyses at Huntington Park between 0800 and 1300 PST
Total C_5 - C_{10} Hydrocarbon >100 ppb

Dependent Variable	Independent Variable(s)	Correlation Coefficient
Time	1,2,4-TMB/Σ 3 HC	0.76
Time	1,2,4-TMB/Σ 3 HC, Oxidant, Σ 3 HC	0.86

when the data points between 0800 and 1300 PST were tested than when all data after 0800 were used. This appeared to be caused by a decrease in photochemical age after the sea breeze front passed. Correlation was also better when the sum of the three hydrocarbons was employed instead of ethylbenzene alone. The highest coefficient was 0.61. The data points with high residuals (outliers) usually occurred on days with low ultraviolet radiation due to heavy clouds or high dispersion rates due to persistent high winds. Significant photochemical reactions prior to 0800 PST were noted occasionally.

Multiple linear regressions involving total oxidant and hydrocarbon concentration in addition to the above parameters produced correlation coefficients as high as 0.76. Finally, restricting the data to the 32 points where the total C_5 to C_{10} hydrocarbons exceeded 100 ppb resulted in the highest correlation. The relationship was:

$$\text{Time (hr)} = -23.1(1,2,4\text{-TMB}/\Sigma 3\text{HC}) + 0.11\ \text{Ox (pphm)} - 0.0042\ \Sigma 3\text{HC (ppb)} + 3.42$$

Correlation Coefficient = 0.86

Standard Error of Estimate = 0.70 hr

The coefficient of 0.11 for oxidant means that the apparent photochemical age was 0.11 hour greater for each 1 pphm increase in oxidant. The relationship also indicates that at any given time the average percent of 1,2,4-TMB reacted was 3% greater for each pphm of oxidant present. This evidence that on high oxidant days hydrocarbons and other contaminants remain in the lower atmosphere for approximately one hour longer for each 10 pphm of additional oxidant provides quantitative confirmation of a generally accepted concept of smog formation.

2.7 TRANSPORT OF POLLUTANTS

The transport of pollutants within the Los Angeles Basin atmosphere occurs in both the horizontal and vertical directions. The importance of horizontal transport has been recognized for many years since it was found that peak oxidant concentrations usually occurred in locations downwind from areas of high pollutant emissions. Pollutants from the Los Angeles area are frequently transported as far as the Riverside - San Bernardino area by late afternoon, a distance in excess of fifty miles. The air monitoring stations at which oxidant concentrations exceed 15 pphm the greatest length of time are those at Azusa, Pomona and Pasadena. These locations are from 10 to 20 miles from downtown Los Angeles and all lie in the northeast quadrant.

During the field survey, the meteorological phenomenon which was primarily responsible for horizontal transport on high oxidant days was the sea breeze which started during late morning. The sea breeze was generated by uneven heating of land and water. Its direction always lay in the southwest quadrant, and its typical mid-afternoon speed was 7 to 8 mph. After sunset the wind speed decreased to 3 mph or less, and its direction shifted to the northeast or southeast quadrants and remained there overnight. During the morning traffic peak (0600 to 0800 PST) the wind speed was generally 2 mph or less and its direction was variable. Little horizontal transport occurred and the pollutants remained in the vicinity of their sources. While other wind patterns such as Santa Ana conditions occurred on low oxidant days, the pattern described above was typical of all high oxidant days in the 1968 field survey.

El Monte was selected as the site for one of the laboratory trailers because it was located in the normal sea breeze trajectory from the primary

site at Huntington Park and in the general area where highest oxidant levels were frequently recorded. Some ozone was produced at El Monte by photochemical reactions involving the pollutants emitted in the immediate vicinity, but the total oxidant prior to the sea breeze never exceeded 14 pphm and was usually less than 10 pphm. On October 23 when the start of the sea breeze was delayed, the oxidant concentration at El Monte remained in the 12 to 14 pphm range for 3 hours before passage of the smog front. This appeared to be the maximum oxidant that could be produced from emissions at levels present in the El Monte area.

The passage of the smog front through El Monte shortly after the onset of the sea breeze was clearly evident. It was more obvious from the rapid oxidant increase shown on the continuous strip charts than from the half hour oxidant averages. The passage of the smog front, representing the boundary of the highly polluted air mass from the downtown area, was marked by a rapid increase in oxidant of 10 to 25 pphm. Other contaminants including hydrocarbons and carbon monoxide also increased sharply. It is unfortunate that continuous data for these parameters were not available so that the rate and magnitude of increase of contaminants could be compared to that for oxidant and ozone. However, these data were obtained in the 1969 survey.

The oxidant maximum was reached from one to two hours after the front passed. The relatively rapid decrease in oxidant after the maximum is generally attributed to a decrease in overall pollution levels after the main polluted air mass has passed on to the east. This seems to explain the decrease during the first half hour to hour after the maximum, but the large decrease during the period from 1400 to 1600 PST is more likely the result of the reduction of ultraviolet radiation intensity by a factor of three and

inhibition from the nitric oxide in fresh emissions which increase as the afternoon traffic density increases.

The contaminant concentrations found at El Monte after passage of the smog front were lower than found during the early morning peak. The airborne data indicated that the vertical distribution was quite uniform up to 1500 to 2000 feet MSL during the sea breeze, but that there were large differences between ground level concentrations and those aloft during the morning.

A comparison of contaminant concentrations at Huntington Park at the time the sea breeze started with those found at El Monte after the smog front passed showed a slight decrease in contaminant concentrations but a large increase in oxidant. The oxidant increase was greater than would be expected if the air mass had remained at Huntington Park.

2.8 AIRBORNE MEASUREMENTS

The airborne measurements made during the 1968 field survey represented a pioneering effort in the exploration of the three-dimensional aspects of the Los Angeles Basin atmosphere. A considerable amount of new knowledge about vertical pollutant patterns was gained, but as is the case in most initial efforts, a number of shortcomings in the flight plans were found during the data analysis. The experience gained in the 1968 program provided a sound basis for designing the airborne phase of the 1969 program which yielded a wealth of information on the complex three-dimensional structure of a 20 mile cross-section of the Basin atmosphere. In order to derive the most information from the 1968 data, reference has been made to the 1969 data in areas which were not covered in 1968. This permitted a

more complete explanation of the 1968 data.

The vertical profiles showed that an inversion existed during the morning on nearly all days in the test period. On a typical day the layer of air from ground level to approximately 700 feet above sea level showed a relatively constant vertical temperature. Above this was a zone where the temperature increased with altitude. This inverted layer was very stable, and the contaminants emitted at ground level mixed only to the base of the inversion. Thus, in the lowest layer fresh emissions were mixed and irradiated, and photochemical reactions initiated. This is much clearer in the 1969 data where air samples were collected in the lower layer, whereas in 1968 most morning samples were collected above the inversion base.

The air within the inversion from perhaps 700 to 2500 feet MSL contained contaminants most of which were probably emitted during the previous day. Thus, while the concentrations were quite low, the photochemical age of the air mass was sufficient for oxidants to begin to form almost immediately upon irradiation. This resulted in higher early morning oxidant levels above the inversion base than below it where the nitric oxide in fresh emissions inhibited oxidant formation until mid-morning or later. The analyses of the bag samples collected above the inversion base frequently showed substantial amounts of hydrocarbons from the exhaust of piston engine aircraft. This is typefied by the high concentrations of C_5 to C_8 branched-chain paraffins and C_7 and C_8 aromatics. The 1969 data show that this hydrocarbon composition is not representative of the atmosphere in general. Aircraft exhaust was found in the 1968 samples because the patterns flown to collect bubbler samples for nitrogen oxides determination resulted in flights in areas frequented by other aircraft.

As a typical day progressed, oxidant increased rapidly in the ground layer and the inversion base started to rise. The sea breeze then began and it transported the polluted air from the downtown area toward El Monte. The smog front was clearly visible from aloft. Smog fronts were traversed on several occasions, and it was found that oxidants were higher at the leading edge than within the clouds. Visible voids containing very low oxidant were also observed within the clouds. The rapid mixing which took place at this time prevented the accumulation of aircraft exhaust, and the chromatograms of samples taken at 1500 feet were barely distinguishable from those of ground level air. At times the inversion disappeared completely, the temperature followed the adiabatic lapse rate, and the oxidant changed little from ground level to 2500 feet. At other times the inversion remained at high altitudes and a sharp decrease in oxidant was noted between 1500 and 2000 feet. At the interface the combination of updrafts containing high oxidant ($\sim$30 pphm) and downdrafts containing low oxidant ($\sim$10 pphm) kept the needle of the oxidant recorder moving continuously.

The substantial differences in afternoon profiles for points different distances from the ocean and the extreme complexity of the overall system are demonstrated much more clearly in the 1969 data. The 1968 data is basically valid, but it does not cover a broad enough area to permit an understanding of its total meaning. Nevertheless, the background knowledge that it provided was absolutely essential to the success of the 1969 airborne program.

3. IMPROVEMENT OF ANALYTICAL METHODS FOR ATMOSPHERIC POLLUTANTS

The work to improve analytical methods used in the 1968 atmospheric studies was directed to the determination of organic nitrogen compounds, hydrocarbons, nitrogen oxides, oxidants and ozone. The primary objectives were to improve techniques which did not produce satisfactory results or devise alternate methods and to expand other procedures so they would provide additional useful data.

3.1 ORGANIC NITROGEN COMPOUNDS

The organic nitrogen compounds known to be produced in photochemical reactions belong to two classes: alkyl nitrates and peroxyacyl nitrates. Emphasis was placed upon determination of peroxyacyl nitrates which are present in objectionable concentrations. While these compounds are present in low parts per billion concentrations in the atmosphere, they are of great interest because of the manifestations associated with them. Peroxyacetyl nitrate (PAN) is present in greater concentrations than its higher homologs, and it is usually the only peroxyacyl nitrate determined. However, its homologs, including peroxypropionyl nitrate (PPN) and peroxybutyryl nitrate (PBN) have been shown to be more powerful eye irritants and phytotoxicants than PAN. The recently discovered peroxybenzoyl nitrate (PBzN) has been found to be 200 times as potent an eye irritant as formaldehyde[14].

The three major sub-tasks related to organic nitrogen compound analysis were improvement and expansion of the analytical technique employing a gas chromatograph equipped with an electron capture detector, development of a stable calibration standard and automation of the analytical system.

ANALYTICAL PROCEDURE FOR PAN

Difficulties were experienced in the 1968 field survey in obtaining

a response to low concentrations of PAN using the Varian Aerograph Hy Fi III Chromatographs. The columns had been found satisfactory on another instrument in laboratory tests performed prior to the field work. The procedure was now checked out in the laboratory using the chromatograph from the Scott field trailer. PAN was produced in a photochemical reactor and transferred to the 40 meter long path cell of a Perkin-Elmer Model 21 Infrared Spectrophotometer. The concentration was determined from the absorption peak at 12.6 microns using the molar absorptivity reported by Stephens[15]. Samples were withdrawn in glass syringes, diluted to parts per billion concentrations and injected into the chromatograph. The problem of loss of PAN within the instrument was traced to the injection block. When the flow system was revised to bypass the injection block so that the sample passed directly from the sampling loop to the chromatographic separation column, no losses of PAN were evident.

The overall system was optimized and the following conditions were selected for field use:

Column: 23' x 1/8" Teflon packed with 5% Carbowax 400 on Diaport S

Carrier gas: Nitrogen at 65 cc/min (80 psig)

Column Temperature: 35°C

Detector Temperature: 100° C

Injection Temperature: Ambient

Sample Size: 5 cc

At these conditions PPN was eluted immediately after PAN and its concentration could be determined if it exceeded one part per billion. Unfortunately, no suitable method for low parts per billion concentrations of PBzN was developed in time for use in the 1969 field program.

CALIBRATION STANDARD FOR ELECTRON CAPTURE DETECTOR

The response of the electron capture detector changes from day to day as the detector cell becomes contaminated. A working calibration standard is needed for daily adjustment but PAN is unstable in pressurized containers. The alternative which was explored was the use of a more stable compound which would elute from the column in the vicinity of PAN and produce a detector response proportional to that of PAN. Propyl nitrate was chosen from a list of candidate compounds and a pressurized cylinder was prepared at a concentration of 5 ppb. The ratio of PAN response to propyl nitrate response was the same from day to day and the concentration of propyl nitrate appeared sufficiently stable for field use. A calibration curve for PAN in terms of the propyl nitrate standard is required at the beginning of a test program and rechecking is desirable occasionally thereafter, but propyl nitrate appeared satisfactory for daily calibration of the electron capture detector.

AUTOMATION OF PAN CHROMATOGRAPH

The Varian Aerograph Chromatographs were automated by the addition of appropriate solenoid valves and timers. Analyses for PAN were then performed at 20 minute intervals on a 24 hour basis. This was done to follow PAN concentrations past normal working hours since it had been reported that PAN persisted well into the night[16].

3.2 HYDROCARBONS

The analytical procedure for individual C_1 to C_{10} hydrocarbons developed for use in the 1968 field survey made possible for the first time the acquisition of data for the complete range of hydrocarbons present in

the atmosphere. The procedure employed a Perkin-Elmer Model 900 Chromatograph with dual flame ionization detectors and a sub-ambient accessory. A packed column was used to separate the C_1 to C_4 hydrocarbons and a capillary column was used to separate the C_5 to C_{10} compounds. Concentrations of less than 0.1 ppb could be detected using a 25 ml sample. The problems encountered in performing the hydrocarbon analyses included interference from hydrocarbon impurities present in the helium carrier gas, an unstable baseline for the packed column during temperature programming and hang-up of high molecular weight components in the inlet system of the chromatograph.

PURIFICATION OF CARRIER GAS

A catalytic purifier was designed and constructed to remove the trace hydrocarbons from the carrier gas. The catalyst bed was composed of 60/80 mesh copper oxide operated at 650 to 700° C. It was followed by a molecular sieve trap to remove water and carbon dioxide. This purifier worked well in the laboratory with all grades of helium. It also removed the methane from a gas mixture containing 2 ppm in air.

The problem of high molecular weight compound contamination was traced to the diaphragm and inserts in the flow controller and flow meter upstream from the gas sampling valve. The small in-line molecular sieve trap became overloaded and the material bled through to the capillary column and eluted as a large broad peak. Frequent reactivation of the molecular sieve trap by heating was found to be necessary to keep the undesired material out of the system.

C_1 to C_4 HYDROCARBON ANALYSIS

The baseline obtained with the Porapak Q - silica gel column used to separate the C_1 to C_4 hydrocarbons was frequently unstable to the point

that certain compounds could not be read accurately. This was attributed to physical changes in the column material during temperature programming. A number of alternate substrates including carbon coated with Apiezon, Polypak-1 and Porapak Q proved unsatisfactory when tested. Finally a column packed with Baymal (colloidal alumina) produced the desired separation. The following conditions were found compatible with the temperature program used with the capillary column:

Column: 12' x 1/8" s.s. packed with 40/80 mesh Baymal

Carrier: Helium @ 75 psig

Fuel: Hydrogen @ 18 psig

Purge: Oxygen @ 40 psig

Sample Size: 25 ml

Temperature Program: Hold column at -75° C for 5 minutes, inject sample, after one minute increase temperature to -20° C and hold for one minute, then program at 6.5°/ min to 120° C and hold. Backflush column after pentane elutes.

HYDROCARBON STABILITY IN TEDLAR BAGS

The stability of hydrocarbons in Tedlar bags was investigated in order to determine if bags collected on high oxidant days could be held for several days before analysis without significant changes in hydrocarbon concentrations. It was found that bags analyzed periodically over several days exhibited only minor changes, with the largest losses occurring in high molecular weight aromatics.

Work was also performed to identify additional peaks in the capillary column chromatograms with emphasis on C_9 and C_{10} aromatics and other high molecular weight compounds.

3.3 NITROGEN OXIDES

The obvious need for more frequent data points for nitrogen oxides at both sites made it necessary to construct new multiple gas samplers. The design of the original BBN sampler was modified to accomodate a set of sixteen bubblers, eight for nitrogen dioxide and eight for nitric oxide. Syringe needles were used as orifices to control the sample flow rates. Two or more samples could be collected simultaneously with each of the completed samplers. Through the use of overlapping sampling periods it was possible to obtain data points at ten minute intervals while still sampling for as long a period as needed to develop sufficient color intensity for accurate results.

NITROGEN OXIDE STABILITY IN TEDLAR BAGS

During the 1968 program nitrogen oxide samples were collected aloft using a manual sampler similar to those employed on the ground. This prodcedure was not satisfactory because pressure changes caused liquid flow between bubblers at times, and the required 15 minute sampling time seriously hindered the profile exploration.

The stability of nitrogen oxides in Tedlar bags was investigated with the idea of extending their successful use for hydrocarbons and carbon monoxide to nitrogen oxides. Several mixtures of nitric oxide and nitrogen dioxide at concentrations in the range of 10 to 30 pphm were used to fill a series of 6-liter Tedlar bags. At each level, five duplicate bags were analyzed at intervals from 0 to 40 hours after filling. Losses averaged 0.1 pphm/hr for nitric oxide and 0.2 to 0.3 pphm/hr for nitrogen dioxide. It was concluded that bags were applicable to nitrogen oxides sampling aloft, but that all bags should be analyzed on the day they are collected.

BECKMAN ACRALYZERS

The Beckman Acralyzers, which had been delivered after the conclusion of the 1968 field survey, were installed in the government-owned trailer. The permanganate solution normally used to oxidize nitric oxide to nitrogen dioxide was replaced with a more efficient and reliable solid chromic oxide oxidizer. A cold trap was placed ahead of the oxidizer to remove aerosols carried over from the first absorption column which would have shortened the oxidizer's life substantially. The modified oxidizer unit performed quite well, but the sensitive pressure balance of the liquid-gas system necessitated additional modifications to achieve proper flows through the instrument.

3.4 OXIDANTS AND OZONE

The analyses for oxidant and ozone in the 1968 programs lent some support to laboratory chamber findings of oxidants other than ozone in photochemical systems[17]. These include hydrogen peroxide and alkyl hydroperoxides. The methods reported in the literature for these compounds were found unsatisfactory for use in the 1969 field program because too much time would have been required each day to set them up and perform them. The 1,2-di-(4-pyridyl) ethylene (DBE) method[18] for ozone was found to be useful for checking the Mast Oxidant Recorder calibration. Air was sampled from the vicinity of a Xenon lamp to obtain the required ozone. The Mast instrument was operated in parallel with the midget impingers used in the DBE method. The results from the instrument and the colorimetric procedure agreed within 1 to 2 pphm in the range from 20 to 40 pphm ozone.

The Mast oxidant analyzers used in the field program included olefin titration apparatus to determine ozone. The ozone was removed by

addition of trans-2-butene in alternate 7 1/2 minute cycles. The concentration of ozone was indicated by the difference between the oxidant reading without addition of trans-2-butene and that with addition of trans-2-butene. The olefin titration apparatus was rebuilt and the on-off cycles were increased from 7 1/2 to 15 minutes each. This made it possible to better observe the oxidant fluctuations within each cycle and resulted in less total dead time during cycle changes.

The Beckman Acralyzer for oxidant received after completion of the 1968 field work was installed in the Government-owned trailer. It served as a supplement to the Mast Recorder.

3.5 MISCELLANEOUS

The substantial number of defects found in new equipment obtained for the 1968 survey and the frequent failures experienced after a short term of operation made it desirable to check out all new equipment as soon as it was received. Some instrumentation used in the 1968 field work had been obtained on a loan basis with new units supplied when available. Other equipment was received from the sub-contractor, Bolt, Beranek and Newman at the conclusion of their effort. The items which were checked included the Eppley Radiation Photometers, Climet Temperature and Dew Point System, Bendix Hydro-Thermographs, Gas Samplers, etc. The number of defects found made it well worth the effort to carry out this task. Corrective action was taken so that the equipment was operational by the start of the 1969 field program.

4. DISCUSSION AND RECOMMENDATIONS

The analysis of the aerometric data collected in the Los Angeles Basin in the Fall of 1968 has produced valuable information regarding the composition of the atmosphere and the rates of the reactions which take place in it. It was not possible to prove the validity of the hypothesized relationships between the system inputs and its outputs because of an insufficient number of data points for certain inportant parameters. Nevertheless, the data provide sufficient insight into atmospheric behavior to permit a better understanding of the quantitative aspects of smog formation.

The data analysis suggested that a number of sources contributed to the various contaminants found in the atmosphere. Detailed analyses of the various sources, especially for C_1 to C_{10} hydrocarbons, is necessary in order to firmly establish the quantity of contaminants emitted by each source. This information is needed to determine the value of applying potential source controls.

The relatively good agreement between the observed rates of formation of nitrogen dioxide and ozone and the values calculated from laboratory results was encouraging. Most data appeared to support the findings of laboratory studies when the laboratory work employed test chamber systems which resembled the atmospheric system. The major difference noted between the atmosphere and laboratory work was in the behavior of nitrogen oxides. In the atmosphere the concentration of total nitrogen oxides changes primarily by dilution as shown by the relatively constant within day CO/NO_x and HC/NO_x ratios. On the other hand, laboratory systems frequently exhibit large losses of nitrogen oxides with time, probably through reactions on the chamber walls.

The formation rates of photochemical products were favored by high contaminant concentrations. It also appeared that the formation rates were inhibited by fresh emissions. If this was true, then the actual rates represent the net effect of the driving force of the reactants and the inhibiting force of new emissions. This can account for the relatively high oxidant concentrations found in remote areas and aloft. The reactant concentrations are low but inhibition is negligible, and oxidant formation can proceed at a moderate rate.

The low concentrations of fuel range olefins found at the start of photochemical activity are of considerable importance. The calculation of nitrogen dioxide formation rates suggests that these olefins are minor contributors to photochemical products. If the assumptions made are valid, proposed fuel modifications would not have a great effect on the rate of chemical and photochemical reactions in the atmosphere.

The approach used in analyzing the data, namely seeking empirical relationships between the inputs and outputs of the atmospheric system, gave evidence of being very useful in developing the mathematical expressions needed to evaluate proposed control measures applicable to the system inputs. In order to fully explore this approach, it is recommended that simultaneous, comprehensive data be obtained for all of the pertinent parameters. The parameters include: nitric oxide, nitrogen dioxide, individual hydrocarbons, ozone, total oxidant, ultraviolet radiation intensity, temperature and humidity. It is desirable that the data points be as frequent as practical so that accurate reaction rates can be determined. Additional vertical profile data is also needed to obtain a three--dimensional view of the atmosphere and the reactions and transport of pollutants which take place in it.

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